

# Conjugated diene compound polymerization catalyst, process for the preparation of conjugated diene polymer in the presence thereof and polybutadiene thus prepared

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**Applicant(s):** UBE INDUSTRIES [JP]

**Classification:**


- international: C08F4/68; C08F10/00; C08F36/04; C08F4/639; C08F4/00; C08F10/00; C08F36/00; C08F4/00; (IPC1-7): C08F36/06; C08F4/60


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## Abstract of TW 475938 (B)

The present invention provides a process for the production of a conjugated diene polymer having a controlled microstructure at a high polymerization activity in the presence of a metallocene type complex of compound of transition metal of the group V of the Periodic Table. A novel catalyst is provided comprising (A) a metallocene type complex of a transition metal of the group V of the periodic table, (B) an ionic compound of a non-coordinating anion and a cation, (C) an organic metal compound of the groups I to III and (D) water, wherein the molar ratio of (C)/(D) is from 0.66 to 5.; A novel process for the production of a conjugated diene polymer is also provided, which comprises the polymerization of a conjugated diene compound in the presence of a catalyst comprising (A) a metallocene type complex of a transition metal of the group V of the periodic table, (B) an ionic compound of a non-coordinating anion and a cation, (C) an organic metal compound of the groups I to III and (D) water, wherein the molar ratio of (C)/(D) is from 0.66 to 5.

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[44]中華民國 91 年 (2002) 02 月 11 日

發明

全 2 頁

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C08F36/06

[54]名稱：共軛二烯化合物之聚合觸媒、在該觸媒之存在下製造共軛二烯聚合物之方法、及所製得之聚丁二烯

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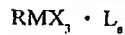
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[57]申請專利範圍：

1. 一種觸媒，包含：

(A)週期表 V 族過渡金屬之金屬茂型錯合物，其為如下通式代表之化合物：



其中 R 為環戊二烯基，經取代環戊二烯基、苄基、經取代苄基、苄基或經取代苄基；M 為 V 族過渡金屬；X 為氫原子、鹵原子、C<sub>1-20</sub> 烷基、烷氧基或胺基；L 為劉易士鹼；a 為 0，1 或 2；

或如下通式代表之化合物：



其中 R 為環戊二烯基，經取代環戊二烯基、苄基、經取代苄基、苄基或經取代苄基；M 為 V 族過渡金屬；L 為劉

易士鹼；a 為 0，1 或 2；

(B)包含非配位陰離子與陽離子之離子化合物，該非配位陰子係選自包括：

四(苯基)硼酸鹽、四(氟苯基)硼酸鹽、四(二氟苯基)硼酸鹽、四(三氟苯基)硼酸鹽、四(四氟苯基)硼酸鹽、四(五氟苯基)硼酸鹽、四(四氟甲基苯基)硼酸鹽、四(3,5-雙三氟甲基苯基)硼酸鹽、四(甲苯基)硼酸鹽、四(二甲苯基)硼酸鹽、三(五氟苯基)(苯基)硼酸鹽、三十氫化物-7,8-二卡巴十二硼酸鹽、四氟硼酸鹽及六氟磷酸鹽之集團；該非配位陽離子係選自包括：碳鎢陽離子、氧鎢陽離子、鉍陽離子、鎂陽離子、環庚三

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烯陽離子及含有過渡金屬之銻鐵陽離子之集團；

(C)週期表 I-III 族元素之有機金屬化合物，

其係選自包括有機鋁化合物、有機鋰化合物、有機鎂化合物、有機鋅化合物及有機硼化合物之集團；

(D)水；

其中(C)/(D)之莫耳比為 0.66 至 5。

- 2.根據申請專利範圍第 1 項之觸媒，其中該週期表 V 族過渡金屬為鈮。
- 3.根據申請專利範圍第 1 項之觸媒，其中該週期表 I-III 族元素為鋁。
- 4.一種製備共軛二烯聚合物之方法，其包括在根據申請專利範圍第 1 項所定義之觸媒存在下由共軛二烯化合物進行聚合。
- 5.根據申請專利範圍第 4 項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用在氬存在下進行。
- 6.根據申請專利範圍第 4 項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用係進行本體聚合作用。
- 7.根據申請專利範圍第 4 項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用係在作為溶劑之芳香化合物中進行。
- 8.根據申請專利範圍第 4 項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用係在作為溶劑之脂系化

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合物中進行。

- 9.根據申請專利範圍第 4 項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用係在作為溶劑之 2-丁烯中進行。
- 10.根據申請專利範圍第 4 項之製備共軛二烯聚合物之方法，其中該共軛二烯化合物為主要由丁二烯所組成之共軛二烯化合物。
- 11.根據申請專利範圍第 10 項之製備共軛二烯聚合物之方法，其中該週期表 I 至 III 族之有機金屬化合物(C)與該水(D)已事先互相接觸。
- 12.根據申請專利範圍第 10 項之製備共軛二烯聚合物之方法，其中該(C)/(D)之莫耳比為 0.7 至 1.5。
- 13.根據申請專利範圍第 10 項之製備共軛二烯聚合物之方法，其中在聚合作用之前，先在不超過 40°C 之溫度下，與觸媒成份接觸 1 至 60 分鐘。
- 14.根據申請專利範圍第 10 項之製備共軛二烯聚合物之方法，其中構成共軛二烯聚合物之丁二烯中 1,2-結構單元、順式-1,4-結構單元及反式-1,4-結構單元之含量分別為 4 至 30 莫耳%，65 至 95 莫耳%及不超過 5 莫耳%，且甲苯溶液黏度( $T_{cp}$ )對門尼黏度(Mooney viscosity)在 100°C 下( $ML_{1+4}$ )之比例( $T_{cp}/ML_{1+4}$ )為 2 至 6。
- 25.
- 30.

**PATENT BULLETIN OF REPUBLIC OF CHINA**  
**(TRANSLATION)**

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Date: 11 February 2002

Invention

Pages: 2

Int. Cl.<sup>7</sup> : C08F4/60

<sup>7</sup> C08F36/06

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Title of Invention: Conjugated diene compound polymerization catalyst, process for the preparation of conjugated diene polymer in the presence thereof and polybutadiene thus prepared

Application No.: 087119271

Filing Date: 20 November 1998

Priority: JP 322543

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Japan

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HOSOYAMA YOSHIHIRA

Japan

YUASA SAKAE

Japan

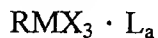
Applicant: UBE INDUSTRIES LTD.

Japan

Attorney, Agent, or Firm: Chang-Wen Chen

Claims:

1. A catalyst comprising (A) a metallocene type complex of a transition metal of the group V of the Periodic Table, which is a compound represented by the following general formula:



wherein R represents a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group or a substituted fluorenyl group; M represents a compound of the group V transition metal; X represents a hydrogen atom, a halogen atom, a C<sub>1-20</sub> hydrocarbon group, an alkoxyl group or an amino group; L represents a Lewis base; and a represents 0, 1 or 2; or which is a compound represented by the following general formula:

RM · L<sub>a</sub>

wherein R represents a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group or a substituted fluorenyl group; M represents a compound of the group V transition metal; L represents a Lewis base; and a represents 0, 1 or 2;

(B) an ionic compound of a non-coordinating anion and a cation, wherein the non-coordinating anion is selected from the group composed of tetra(phenyl)borate, tetra(fluorophenyl)borate, tetrakis(difluorophenyl)borate, tetrakis(trifluorophenyl)borate, tetrakis(tetrafluorophenyl)borate, tetrakis(pentafluorophenyl)borate, tetrakis(tetrafluoromethylphenyl)borate, tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tetra(tolyl)borate, tetra(xylyl)borate, triphenyl(pentafluorophenyl)borate, tris(pentafluorophenyl)(phenyl)borate, tridecahydride-7,8-dicarbaundecaborate, tetrafluoroborate, and hexafluorophosphate; the non-coordinating cation is selected from the group composed of carbonium cation, oxonium cation, ammonium cation, phosphonium cation, cycloheptatrienyl cation, and ferrocenium cation containing transition metal;

(C) an organic metal compound of an element of the groups I to III of the Periodic Table, which is selected from the group composed of organic aluminum compound, organic lithium compound, organic magnesium compound, organic zinc compound, and organic boron compound;

(D) water;

wherein the molar ratio of (C)/(D) is from 0.66 to 5.

2. The catalyst according to any one of Claims 1, wherein said transition metal of the group V of the Periodic table is vanadium.
3. The catalyst according to any one of Claims 1, wherein said element of the groups I to III of the Periodic table is aluminum.
4. A process for the preparation of a conjugated diene polymer, which comprises polymerizing a conjugated diene compound in the presence of a catalyst defined in any one of Claims 1.
5. The process for the preparation of a conjugated diene polymer according to Claim 4, wherein the polymerization of a conjugated diene compound is effected in the presence of hydrogen.
6. The process for the preparation of a conjugated diene polymer according to Claim 4, wherein the polymerization of a conjugated diene compound is carried out by bulk polymerization.
7. The process for the preparation of a conjugated diene polymer according to Claim 4, wherein the polymerization of a conjugated diene compound is effected in an aromatic compound as a solvent.
8. The process for the preparation of a conjugated diene polymer according to Claim 4, wherein the polymerization of a conjugated diene compound is effected in an

aliphatic compound as a solvent.

9. The process for the preparation of a conjugated diene polymer according to Claim 4, wherein the polymerization of a conjugated diene compound is effected in 2-butene as a solvent.
10. The process for the preparation of a conjugated diene polymer according to any one of Claims 4, wherein said conjugated diene compound is a conjugated diene compound mainly composed of butadiene.
11. The process for the preparation of a conjugated diene polymer according to Claim 10, wherein said organic metal compound of the groups I to III of the Periodic table (C) and said water (D) have previously been allowed to come in contact with each other.
12. The process for the preparation of a conjugated diene polymer according to Claim 10, wherein said molar ratio of (C)/(D) is from 0.7 to 1.5.
13. The process for the preparation of a conjugated diene polymer according to Claim 10, wherein the polymerization is preceded by the contact with a catalyst component at a temperature of not higher than 40°C for 1 to 60 minutes.
14. A polybutadiene obtained by the process for the preparation of a conjugated diene polymer according to Claim 10, wherein the content of 1,2-structure unit, cis-1,4-structure unit and trans-1,4-structure unit in the butadiene monomer unit are from 4 to 30 mol%, from 65 to 95 mol% and not more than 5 mol%, respectively, and the ratio ( $T_{cp}/ML_{1+4}$ ) of toluene solution viscosity ( $T_{cp}$ ) to Mooney viscosity at 100°C ( $ML_{1+4}$ ) is from 2 to 6.

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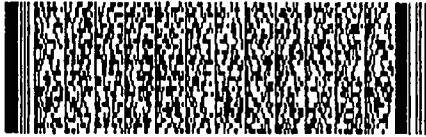
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<b>公 告 本</b>		<b>發明專利說明書</b>	475938
一、 發明名稱	中 文	共軛二烯化合物之聚合觸媒、在該觸媒之存在下製造共軛二烯聚合物之方法、及所製得之聚丁二烯	
	英 文	CONJUGATED DIENE COMPOUND POLYMERIZATION CATALYST, PROCESS FOR THE PREPARATION OF CONJUGATED DIENE POLYMER IN THE PRESENCE THEREOF AND POLYBUTADIENE THUS PREPARED	
二、 發明人	姓 名 (中文)	1. 辻 本 信弘 2. 前田 孝二 3. 村上 真人 4. 鈴木 通典	
	姓 名 (英文)	1. NOBUHIRO TSUJIMOTO 2. KOJI MAEDA 3. MASATO MURAKAMI 4. MICHINORI SUZUKI	
	國 籍	1. 日本 2. 日本 3. 日本 4. 日本	
	住、居所	1. 日本國東京都江戸川区西葛西3-22-45-207 2. 日本國千葉縣茂原市綠丘4-29-8 3. 日本國千葉縣市原市山木44-3 4. 日本國千葉縣市原市地原台3-32-1-1	
三、 申請人	姓 名 (名稱) (中文)	1. 日商宇部興產股份有限公司	
	姓 名 (名稱) (英文)	1. UBE INDUSTRIES, LTD.	
	國 籍	1. 日本	
	住、居所 (事務所)	1. 日本國山口縣宇部市西本町1丁目12番32號	
	代表人 姓 名 (中文)	1. 長廣 真臣	
	代表人 姓 名 (英文)	1.	
 			

申請日期：	案號：
類別：	

(以上各欄由本局填註)

## 發明專利說明書

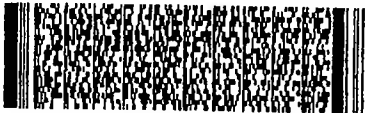
一、 發明名稱	中文	
	英文	
二、 發明人	姓名 (中文)	5. 岩本 泰昌 6. 久野 信治 7. 萬代 智 8. 細山 善平
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	住、居所	5. 日本國千葉縣市原市 社4-11-15 6. 日本國千葉縣市原市山木44-3 7. 日本國千葉縣千葉市中央區川戶町329-17 8. 日本國千葉縣市原市山木44-3
三、 申請人	姓名 (名稱) (中文)	
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	國籍	
	住、居所 (事務所)	
	代表人 姓名 (中文)	
	代表人 姓名 (英文)	
		



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## 發明專利說明書

一、 發明名稱	中文	
	英文	
二、 發明人	姓名 (中文)	9. 湯淺 榮
	姓名 (英文)	9. SAKAE YUASA
	國籍	9. 日本
	住、居所	9. 日本國千葉縣袖浦市蔵波台2-23-6
三、 申請人	姓名 (名稱) (中文)	
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	國籍	
	住、居所 (事務所)	
	代表人 姓名 (中文)	
	代表人 姓名 (英文)	
		

本案已向

國(地區)申請專利	申請日期	案號	主張優先權
日本 JP	1997/11/25	特願平9-322543	有
日本 JP	1998/07/03	特願平10-188943	有
日本 JP	1998/08/25	特願平10-238990	有

有關微生物已寄存於

寄存日期

寄存號碼

無

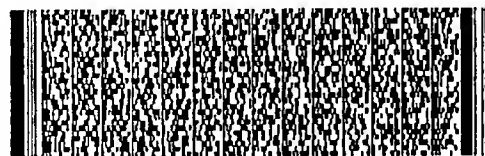


四、中文發明摘要 (發明之名稱：共軛二烯化合物之聚合觸媒、在該觸媒之存在下製造共軛二烯聚合物之方法、及所製得之聚丁二烯)

本發明提供一種在週期表V族之過渡金屬化合物之金屬茂型錯合物存在下，在高聚合活性下，製造具有控制微觀結構之共軛二烯聚合物之方法。並提供一種新穎觸媒，包含(A)週期表V族之過渡金屬的金屬茂型錯合物，(B)非配位陰離子與陽離子之離子化合物，(C)I至III族之有機金屬化合物及(D)水，其中(C)/(D)之莫耳比為0.66至5。亦提供一種製造共軛二烯聚合物之新穎方法，其包括在包括(A)週期表V族之過渡金屬之金屬茂型錯合物，(B)非配位陰離子與陽離子之離子化合物，(C)I至III族之有機金屬化合物及(D)水，(其中(C)/(D)之莫耳比為0.66至5)之觸媒存在下，由共軛二烯化合物進行聚合。

英文發明摘要 (發明之名稱：CONJUGATED DIENE COMPOUND POLYMERIZATION CATALYST, PROCESS FOR THE PREPARATION OF CONJUGATED DIENE POLYMER IN THE PRESENCE THEREOF AND POLYBUTADIENE THUS PREPARED)

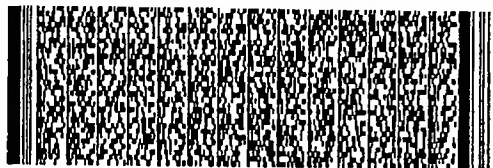
The present invention provides a process for the production of a conjugated diene polymer having a controlled microstructure at a high polymerization activity in the presence of a metallocene type complex of compound of transition metal of the group V of the Periodic Table. A novel catalyst is provided comprising (A) a metallocene type complex of a transition metal of the group V of the Periodic Table, (B) an ionic compound of a non-coordinating anion and a cation, (C) an



四、中文發明摘要 (發明之名稱：共軛二烯化合物之聚合觸媒、在該觸媒之存在下製造共軛二烯聚合物之方法、及所製得之聚丁二烯)

英文發明摘要 (發明之名稱：CONJUGATED DIENE COMPOUND POLYMERIZATION CATALYST, PROCESS FOR THE PREPARATION OF CONJUGATED DIENE POLYMER IN THE PRESENCE THEREOF AND POLYBUTADIENE THUS PREPARED)

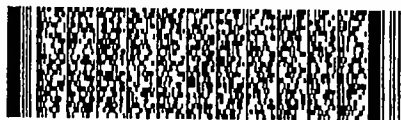
organic metal compound of the groups I to III and (D) water, wherein the molar ratio of (C)/(D) is from 0.66 to 5. A novel process for the production of a conjugated diene polymer is also provided, which comprises the polymerization of a conjugated diene compound in the presence of a catalyst comprising (A) a metallocene type complex of a transition metal of the group V of the Periodic Table, (B) an ionic compound of a non-coordinating anion and a cation, (C) an



四、中文發明摘要 (發明之名稱：共軛二烯化合物之聚合觸媒、在該觸媒之存在下製造共軛二烯聚合物之方法、及所製得之聚丁二烯)

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organic metal compound of the groups I to III and (D) water, wherein the molar ratio of (C)/(D) is from 0.66 to 5.



## 五、發明說明 (1)

發明之領域

本發明係關於一種共軛二烯化合物聚合用之觸媒。特別是，本發明係關於一種製備具有控制微觀結構之聚丁二烯之方法。更特別是，本發明係關於一種具有控制微觀結構與高分子直線型之聚丁二烯。

發明之背景

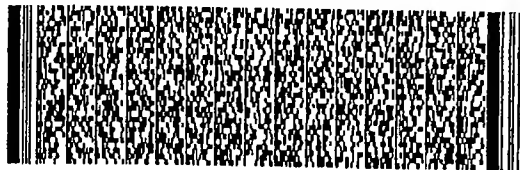
已知當共軛二烯在聚合觸媒存在下聚合時，可得具有各種微觀結構之聚合物。一種自鈷化合物與有機鋁化合物製備具有高順式結構之聚丁二烯之方法為習知方法。具有順式結構包含適量加入其中之1,2-結構之聚丁二烯預期可作為乙烯芳香族聚合物之衝擊改值劑。

近年來，使用金屬茂型錯合物作為觸媒之各種烯烴類之研發正在進行中。共軛二烯之聚合亦有研究。

參照共軛二烯在金屬茂型錯合物存在下之聚合，一種由三氯化環戊二烯鈦( $\text{CpTiCl}_3$ )作為週期表IV族過渡金屬之化合物與甲基鋁噶烷組成之觸媒系統揭示於Macromol. Symp., Vol. 89, 383頁(1995)等。然而，觸媒之缺點為其具有低聚合活性。

JP-B-46-20494("JP-B"一詞意指"已審核日本專利公告案")揭示一種在由 $\text{CpVCl}_3 + (\text{i-C}_4\text{H}_9)_3\text{Al}/\text{AlCl}_3 + \text{H}_2\text{O}$ 組合之觸媒系統存在下製備聚丁二烯之方法。然而，此觸媒系統之缺點在於其具有低聚合活性。

一種使用由鈮(III)化合物如週期表V族之過渡金屬之金屬茂型錯合物(例如， $\text{CpVCl}_2 \cdot (\text{PEt}_3)_2$ ,  $\text{Cp}_2\text{VCl}$ )與甲基鋁



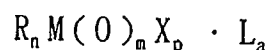
## 五、發明說明 (2)

噶烷組成之觸媒，製備具有順式結構包含10至20%比例加入其中之1,2-結構之聚丁二烯之方法揭示於Polymer, Vol. 37(2), 363頁(1996)。

另外，JP-A-9-202813與JP-A-9-194526("JP-A"一詞意指"未審查公告之日本專利申請案")揭示一種在由具有特定結構與離子化劑之鈮金屬茂化合物組成之觸媒系統存在下製備聚丁二烯之方法。

然而，EP0778291A1揭示一種觸媒包含：

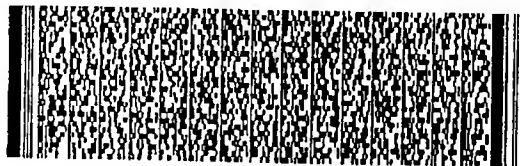
(A) 由下面通式表示之週期表V族之過渡金屬之化合物：



其中M為週期表V族之過渡金屬；R為環戊二烯基，經取代之環戊二烯基、茚基、經取代茚基、芴基或經取代芴基；O為氧原子；X為氫原子、鹵原子、具有1至20個碳原子之烴基、烷氧基、芳氧基或醯胺基；L為劉易士鹼性化合物；n, m及p各為一整數，選擇以作組合(n=1, m=1, p=2), (n=1, m=0, p=3), (n=2, m=0, p=1)或(n=1, m=0, p=2)；及a為0, 1或2及

(B) 至少一個包含非配位陰離子與陽離子之(B1)離子化合物與(B2)鋁噶烷，但其條件為，當該成份(A)之n, m及p之組合為(n=2, m=0, p=1)或(n=1, m=0, p=2)時，該成份(B)為包含非配位陰離子與陽離子之離子化合物(B1)。

聚丁二烯具有所謂微觀結構，其包含在1-及4-位藉聚合



## 五、發明說明 (3)

產生之連接部份(1,4-結構)及在1-及2-位藉聚合產生之連接部份(1,2-結構)，呈現在其分子鏈組合。1,4-結構分成二類型，即，順式結構與反式結構。另一方面，1,2-結構包含乙烯基作為側鏈。

已知具有不同微觀結構之聚丁二烯可視所用之聚合觸媒之種類而製備。此等聚丁二烯視其性質可用於各種目的。

特別是，一種具有微觀結構包含以適量加入有1,2-結構之高順式結構因而幾乎無反式結構及高分子直線性之聚丁二烯具有優異特性如高度耐磨蝕性、高度耐生熱性及高度耐衝擊性。

JP-B-53-44188揭示一種耐衝擊性聚苯乙烯，由具有15至35% 1,2-結構單元含量、20至85%順式-1,4-結構單元含量、20至85%順式-1,4-結構單元含量與50至200 cps之5%苯乙烯溶液黏度(5% SV)之聚丁二烯所組合，但其條件為5%苯乙烯溶液黏度(5% SV)符合下面關係：

$$1.5ML_{1+4} \leq 5\% \text{ 苯乙烯溶液黏度}(5\% \text{ SV}) \leq 3ML_{1+4}$$

通常，5% SV與T<sub>cp</sub>具有5% SV=T<sub>cp</sub> x 1.345關係。因此，提供公式 $1.12 \leq T_{cp}/ML_{1+4} \leq 2.23$ 。

## 發明之概述

因此，本發明之一目的為提供一種在週期表V族之過渡金屬化合物之金屬茂型錯合物所組合之觸媒系統存在下，在高聚合活性下，製備具有控制微觀結構之共軛二烯聚合





## 五、發明說明 (4)

物之方法。

本發明之另一目的為提供一種製備具有微觀結構包含以適量加入有1,2-結構之高順式結構因而在高活性下幾乎無反式結構之聚丁二烯之方法。

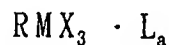
本發明之又一目的為提供一種具有微觀結構與高分子有線性之聚丁二烯。

本發明之此等及其他目的從下列細節說明及實例當可更加明白。

本發明係關於下列組成：

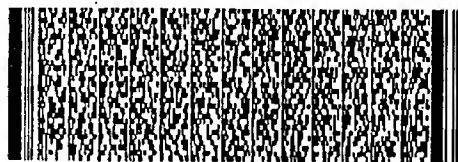
(1) 一種觸媒，包含(A)週期表V族過渡金屬之金屬茂型錯合物，(B)非配位陰離子與陽離子之離子化合物，(C)週期表I至III族元素之有機金屬化合物及(D)水，其中(C)/(D)之莫耳比為0.66至5。

(2) 根據條款(1)之觸媒，其中週期表V族過渡金屬之該金屬茂型錯合物(A)為下面通式表示之化合物：

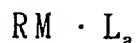


其中R為環戊二烯基，經取代環戊二烯基、茛基、經取代茛基、苄基或經取代苄基；M為V族過渡金屬之錯合物；X為氫原子、鹵原子、 $\text{C}_{1-20}$  烴基、烷氧基或胺基，或為劉易士鹼；及a為0，1或2。

(3) 根據條款(1)之觸媒，其中週期表V族過渡金屬之該金屬茂型錯合物(A)為下面通式表示之化合物：



## 五、發明說明 (5)



其中R為環戊二烯基、經取代環戊二烯基、茚基、經取代茚基、芴基或經取代芴基；M為V族過渡金屬之化合物；L為劉易士鹼；及a為0，1或2。

(4)根據條款(1)至(3)中任一項之觸媒，其中週期表V族之該過渡金屬為鈦。

(5)根據條款(1)至(4)中任一項之觸媒，其中週期表I至III族之該元素為鋁。

(6)一種製備共軛二烯聚合物之方法，其包括在條款(1)至(5)中任一條定義之觸媒存在下聚合共軛二烯化合物。

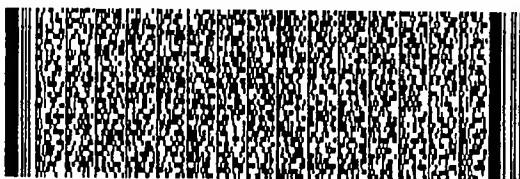
(7)一種製備根據條款(6)之共軛二烯聚合物之方法，其中共軛二烯化合物之聚合在氫存在下實施。

(8)一種製備根據條款(6)或(7)之共軛二烯聚合物之方法，其中共軛二烯化合物之聚合係藉本體聚合實施。

(9)一種製備根據條款(6)或(7)之共軛二烯聚合物之方法，其中共軛二烯化合物之聚合係在芳香化合物作為溶劑中實施。

(10)一種製備根據條款(6)或(7)之共軛二烯聚合物之方法，其中共軛二烯化合物之聚合係在脂系化合物作為溶劑中實施。

(11)一種製備根據條款(6)或(7)之共軛二烯聚合物之方法，其中共軛二烯化合物之聚合係在2-丁烯作為溶劑中實



## 五、發明說明 (6)

施。

(12) 一種製備根據條款(8)或(11)之任一項之共軛二烯聚合物之方法，其中該共軛二烯化合物為主要由丁二烯組成之共軛二烯化合物。

(13) 一種製備根據條款(12)之共軛二烯聚合物之方法，其中週期表(C)I至III族之該有機金屬化合物與該水(D)事先予以互相接觸。

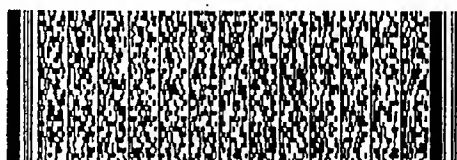
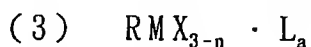
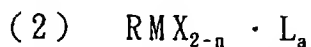
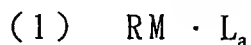
(14) 一種製備根據條款(12)之共軛二烯聚合物之方法，其中該(C)/(D)之莫耳比為0.7至1.5。

(15) 一種製備根據條款(12)之共軛二烯聚合物之方法，其中聚合係在溫度不高於40℃下與觸媒成份接觸1至60分鐘之前。

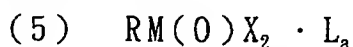
(16) 一種由製備根據條款(12)之共軛二烯聚合物之方法所得之聚丁二烯，其中1,2-結構單元，順式-1,4-結構單元與反式-1,4-結構單元於丁二烯單體單元之含量分別為4至30莫耳%，65至95莫耳%及不多於5莫耳%，甲苯溶液黏度( $T_{cp}$ )對門尼黏度之比( $T_{cp}/ML_{1+4}$ )在100℃( $ML_{1+4}$ )為2至6。

#### 發明之詳細說明

週期表V族過渡金屬化合物之金屬茂型錯合物之例包括由下面通式表示之化合物：



## 五、發明說明 (7)



在式中， $n$  為 1 或 2；及  $a$  為 0，1 或 2。

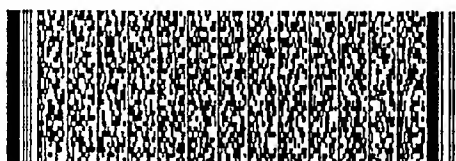
$M$  為週期表 V 族之過渡金屬。過渡金屬之特別例包括鈮 (V)，鈮 (Nb) 及鉭 (Ta)。在此等過渡金屬中較佳者為鈮。

$R$  為環戊二烯基，經取代環戊二烯基、茚基、經取代茚基、苄基或經取代苄基。

在經取代環戊二烯基、經取代茚基或經取代苄基上之取代基之例包括直鏈脂肪烴基或分支脂肪烴基如甲基、乙基、丙基、異丙基、正丁基、異丁基、第二丁基、第三丁基及己基、芳香烴基如苯基、甲苯基、萘基及苄基與具有矽酮原子之烴基如三甲基甲矽烷基。經取代環戊二烯基之另外例包括包含與交聯基連接至  $X$  部份之環戊二烯環者如二甲基甲矽烷基、二甲基亞甲基、甲基苯基亞甲基、二苯基亞甲基、伸乙基及經取代伸乙基。

經取代環戊二烯基之特定例包括甲基環戊二烯基、1,2-二甲基環戊二烯基、1,3-二甲基環戊二烯基、1,3-二(第三丁基)環戊二烯基、1,2,3-三甲基環戊二烯基、1,2,3,4-四甲基環戊二烯基、五甲基環戊二烯基、1-乙基-2,3,4,5-四甲基環戊二烯基、1-苄基-2,3,4,5-四甲基環戊二烯基、1-三甲基甲矽烷基-2,3,4,5-四甲基環戊二烯基及 1-三氟甲基-2,3,4,5-四甲基環戊二烯基。

經取代茚基之特定例包括 1,2,3-三甲基茚基、七甲基茚



## 五、發明說明 (8)

基、及1, 2, 4, 5, 6, 7-六甲基茛基。

經取代茛基之特定例包括甲基茛基。

其中由R表示之較佳基為環戊二烯基、甲基環戊二烯基、五甲基環戊二烯基、茛基及1, 2, 3-三甲基茛基。

X為氫原子、鹵原子、 $C_{1-20}$ 烴基、烷氧基或胺基。X'可相同或相異。

鹵原子之特定例包括氟原子、氯原子、溴原子及碘原子。

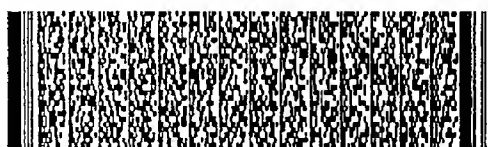
$C_{1-20}$ 烴基之特定例包括直鏈脂肪烴基或分支脂肪烴基如甲基、乙基、丙基、異丙基、正丁基、異丁基、第二丁基、第三丁基及己基，及芳香烴基如苯基、甲苯基、萘基及苄基。 $C_{1-20}$ 烴基之其他例包括具有矽酮原子之烴基如三甲基甲矽烷基。此等 $C_{1-20}$ 烴基中較佳者為甲基、苄基、及三甲基甲矽烷基。

烷氧基之特定例包括甲氧基、乙氧基、苯氧基、丙氧基及丁氧基。烷氧基之其他例包括戊氧基、己氧基、辛氧基、2-乙基己氧基及硫代甲氧基。

胺基之特定例包括二甲基胺基、二乙基胺基及二異丙基胺基。

此等其中由X表示之較佳者為氫原子、氟原子、氯原子、溴原子、甲基、乙基、丁基、甲氧基、乙氧基、二甲基胺基及二乙基胺基。

L為劉易士鹼或標準劉易士鹼性無機或有機化合物，其可被配位至金屬。此等化合物中特佳者為不具活性氫之化



## 五、發明說明 (9)

合物。該化合物之特定例包括醚、酯、酮、胺、膦、烯烴、二烯、芳香烴、炔及甲矽烷氧化合物。

NR' 為亞胺基。R' 為C<sub>1-25</sub>烴取代基。C<sub>1-25</sub>烴取代基之特定例包括直鏈脂肪烴基或分支脂肪烴基如甲基、乙基、丙基、異丙基、第二丁基、第三丁基、己基、辛基及新戊基、及芳香烴基如苯基、甲苯基、萘基、苊基、1-苯基乙基、2-苯基-2-丙基、2,6-二甲基苯基及3,4-二甲基苯基。C<sub>1-25</sub>烴基之其他例包括具有矽酮原子之烴基如三甲基甲矽烷基。

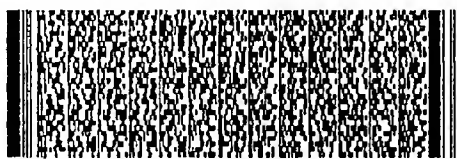
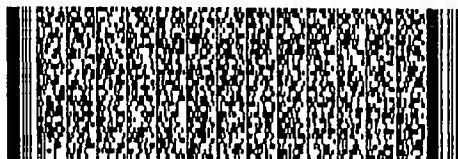
週期表V族過渡金屬化合物之金屬茂型錯合物之例包括下面通式表示之化合物：

- (1)  $RM \cdot L_a$
- (2)  $R_nMX_{2-n} \cdot L_a$
- (3)  $R_nMX_{3-n} \cdot L_a$
- (4)  $RMX_3 \cdot L_a$
- (5)  $RM(O)X_2 \cdot L_a$
- (6)  $R_nMX_{3-n}(NR')$

在此等化合物中較佳者為由前述通式表示之鈮化合物，其中M為鈮，例如， $RV \cdot L_a$ ， $RVX \cdot L_a$ ， $R_2V \cdot L_a$ ， $RVX_2 \cdot L_a$ ， $RVX_3 \cdot L_a$ ， $RV(O)X_2$ ， $RV(NR')X_2$ 。在此等化合物中特佳者為鈮化合物如 $RV \cdot L_a$ 及 $RVX_3 \cdot L_a$ 。

由 $RMX_3$ 表示之化合物之特定例包括下列化合物(i)至(xvi)：

(i) 三氯化環戊二烯鈮



## 五、發明說明 (10)

三氯化環戊二烯鈦之例包括單取代之三氯化環戊二烯鈦如三氯化甲基環戊二烯鈦、三氯化乙基環戊二烯鈦、三氯化丙基環戊二烯鈦、三氯化異丙基環戊二烯鈦、三氯化第三丁基環戊二烯鈦、三氯化(1,1-二甲基丙基)環戊二烯鈦、三氯化(2-基環戊二烯基)鈦、三氯化(1,1-二甲基2-基)環戊二烯鈦、三氯化(3-戊基)環戊二烯鈦、三氯化(3-甲基-3-戊基)環戊二烯鈦、三氯化(二乙基2-基)環戊二烯鈦及三氯化(三甲基甲矽烷基環戊二烯基)鈦。

## (iia) 三氯化1,2-二-取代環戊二烯鈦

三氯化1,2-二-取代環戊二烯鈦之例包括三氯化(1,2-二甲基環戊二烯基)鈦、三氯化(1-乙基-2-甲基環戊二烯基)鈦、三氯化(1-甲基-2-丙基環戊二烯基)鈦、三氯化(1-甲基-2-三甲基甲矽烷基環戊二烯基)鈦、三氯化(1,2-雙(三甲基甲矽烷基)環戊二烯基)鈦、三氯化(1-甲基-2-雙(三甲基甲矽烷基)甲基環戊二烯基)鈦、三氯化(1-甲基-2-戊基環戊二烯基)鈦、三氯化(1-甲基-2-甲苯基環戊二烯基)鈦、三氯化(1-甲基-2-(2,6-二甲基苯基)環戊二烯基)鈦、及三氯化(1-丁基-2-甲基環戊二烯基)鈦。

## (iib) 三氯化1,3-二-取代環戊二烯鈦

三氯化1,3-二-取代環戊二烯鈦之例包括三氯化(1,3-二甲基環戊二烯基)鈦、三氯化(1-乙基-3-甲基環戊二烯基)鈦、三氯化(1-甲基-3-丙基環戊二烯基)鈦、三氯化(1-甲基-3-三甲基甲矽烷基環戊二烯基)鈦、三氯化(1,3-雙(三甲基甲矽烷基)環戊二烯基)鈦、三氯化(1-甲基-3-雙(三



## 五、發明說明 (11)

甲基甲矽烷基)甲基環戊二烯基)釩、三氯化(1-甲基-3-戊基環戊二烯基)釩、三氯化(1-甲基-3-甲基苯基環戊二烯基)釩、三氯化(1-甲基-3-(2,6-二甲基苯基)環戊二烯基)釩、及三氯化(1-丁基-3-甲基環戊二烯基)釩。

(iii) 三氯化1,2,3-三-取代環戊二烯釩

三氯化1,2,3-三-取代環戊二烯釩之例包括三氯化(1,2,3-三甲基環戊二烯基)釩。

(iv) 三氯化1,2,4-三-取代環戊二烯釩

三氯化1,2,4-三-取代環戊二烯釩之例包括三氯化(1,2,4-三甲基環戊二烯基)釩。

(v) 四取代之三氯化環戊二烯釩

四取代之三氯化環戊二烯釩之例包括三氯化(1,2,3,4-四甲基環戊二烯基)釩，及三氯化(1,2,3,4-四苯基環戊二烯基)釩。

(vi) 五取代之三氯化環戊二烯釩

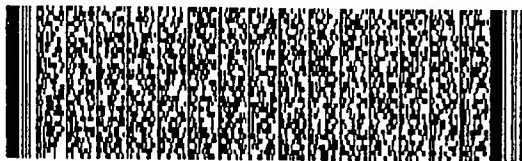
五取代之三氯化環戊二烯釩之例包括三氯化(五甲基環戊二烯基)釩、三氯化(1,2,3,4-四甲基-5-苯基環戊二烯基)釩及三氯化1-甲基-2,3,4,5-四苯基環戊二烯基)釩。

(vii) 三氯化茛基釩

(viii) 經取代之三氯化茛基釩

經取代之三氯化茛基釩之例包括三氯化(2-甲基茛基)釩及三氯化(2-三甲基甲矽烷基茛基)釩。

(ix) 藉烷氧基取代化合物(i)至(viii)中氯原子所得之單醇鹽、二醇鹽及三醇鹽





## 五、發明說明 (12)

此等族群之例包括環戊二烯鈳三(第三丁氧化物)、環戊二烯鈳三(異丙氧化物)、二甲氧氯化環戊二烯鈳、氯化環戊二烯鈳二(異丙氧基)、氯化環戊二烯鈳二(第三丁氧基)、氯化環戊二烯鈳二(苯氧基)、二氯化環戊二烯鈳異丙氧基、第三丁氧二氯化環戊二烯鈳、及苯氧二氯化環戊二烯鈳。

(x) 藉取代化合物(i)至(ix)中氯原子所得之甲基化化合物(xi)包含R互相與烴基或甲矽烷基連接之化合物

此等化合物之例包括二氯化(第三丁基醯胺)二甲基( $\eta^5$ -環戊二烯基)矽烷鈳、二氯化(第三丁基醯胺)二甲基(三甲基- $\eta^5$ -環戊二烯基)矽烷鈳、二氯化(第三丁基醯胺)二甲基(四甲基- $\eta^5$ -環戊二烯基)矽烷鈳。

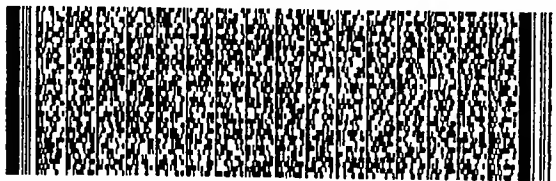
(xii) 藉甲基取代化合物(xi)中氯原子所得之二甲基化化合物

(xiii) 藉烷氧基取代化合物(xi)中氯原子所得之單烷氧化與二烷氧化化合物

(xiv) 藉甲基取代單氯化化合物(xiii)所得之化合物

(xv) 藉醯胺基取代化合物(i)至(viii)中氯原子所得之醯胺化化合物

醯胺化化合物之例包括環戊二烯基(三個二乙基醯胺)鈳、環戊二烯基(三個-異丙基醯胺)鈳、環戊二烯基(三個-異正辛基醯胺)鈳、氯化環戊二烯基(雙二乙基醯胺)鈳、氯化環戊二烯基(雙-異丙基醯胺)鈳、氯化環戊二烯基(雙-正辛基醯胺)鈳、二氯化環戊二烯基(二乙基醯胺)鈳、二



## 五、發明說明 (13)

氯化環戊二烯基(異丙基醯胺)鈦、二氯化環戊二烯基(正辛基醯胺)鈦、(三甲基甲矽烷基環戊二烯基)(三個二乙基醯胺)鈦、(三甲基甲矽烷基環戊二烯基)(三個-異丙基醯胺)鈦、(三甲基甲矽烷基環戊二烯基)(三個-正辛基醯胺)鈦、氯化(三甲基甲矽烷基環戊二烯基)(雙二乙基醯胺)鈦、氯化(三甲基甲矽烷基環戊二烯基)(雙-異丙基醯胺)鈦、氯化(三甲基甲矽烷基環戊二烯基)(雙-正辛基醯胺)鈦、二氯化(三甲基甲矽烷基環戊二烯基)(二乙基醯胺)鈦、二氯化(三甲基甲矽烷基環戊二烯基)(異伸丙基)鈦及二氯化(三甲基甲矽烷基環戊二烯基)(正辛基醯胺)鈦。

(xx) 藉甲基取代化合物(xv)中氯原子所得之甲基化化合物

由 $RM \cdot L_a$ 表示之化合物之特定例包括環戊二烯基(苯)鈦、環戊二烯基(甲苯)鈦、環戊二烯基(二甲苯)鈦、環戊二烯基(三甲基苯)鈦、環戊二烯基(六甲基苯)鈦、環戊二烯基(萘)鈦、環戊二烯基(蒽)鈦、環戊二烯基(芴)鈦、甲基環戊二烯基(苯)鈦、1,3-二甲基環戊二烯基(苯)鈦、1-丁基-3-甲基環戊二烯基(苯)鈦、四甲基環戊二烯基(苯)鈦、五甲基環戊二烯基(苯)鈦、三甲基甲矽烷基環戊二烯基(苯)鈦、1,2-雙(三甲基甲矽烷基)環戊二烯基(苯)鈦、1,3-雙(三甲基甲矽烷基)環戊二烯基(苯)鈦、茚基(苯)鈦、2-甲基茚基(苯)鈦、2-三甲基甲矽烷基茚基(苯)鈦、芴基(苯)鈦、環戊二烯基(伸乙基)(三甲基膦)鈦、環戊二烯基(伸丁基)(三甲基膦)鈦、環戊二烯基(1,4-二苯基伸丁基)(三甲基膦)鈦、環戊二烯基(1,1,4,4-四苯基伸丁



## 五、發明說明 (14)

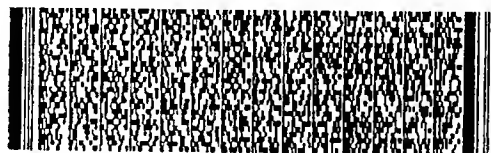
基)(三甲基膦)鈦、環戊二烯基(2,3-二甲基伸丁基)(三甲基膦)鈦、環戊二烯基(2,4-伸己基)(三甲基膦)鈦、環戊二烯基四羰基鈦及茚基四羰基鈦。

由 $R_nMX_{2-n} \cdot L_a$  (其中 $n=1$ )表示之化合物之特定例包括具有其他 $\sigma$ -連接配位體氫原子，鹵原子如氯、溴及碘，烴基如甲基、苯基、 $\alpha$ -基、新戊基、三甲基甲矽烷基及雙三甲基甲矽烷基甲基、烴氧基如甲氧基、乙氧基及異丙氧基或烴胺基如二甲基胺基、二乙基胺基、二-異丙基胺基或二辛基胺基者。

由 $R_nMX_{2-n} \cdot L_a$  (其中 $n=2$ )表示之化合物之特定例包括具有各種環戊二烯基互相與交聯基如 $Me_2Si$ ，二甲基亞甲基、甲基苯基亞甲基、二苯基亞甲基、伸乙基及經取代伸乙基連接者。

可加入由 $R_nMX_{2-n} \cdot L_a$ 表示之化合物中之配位體之其他例包括中性劉易士鹼如烯烴、二烯、芳香烴、炔、胺、醯胺、膦、醚、酮及酯。在此等配位體中較佳者為不具活性氫之劉易士鹼。

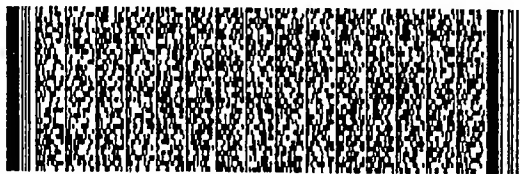
由 $R_nMX_{2-n} \cdot L_a$  (其中 $n=1$ )表示之化合物之特定例包括氯環戊二烯基(四氫呋喃)鈦、氯環戊二烯基(三甲基膦)鈦、氯環戊二烯基雙(三甲基膦)鈦、氯環戊二烯基(1,2-雙二甲基膦基乙烷)鈦、氯環戊二烯基(1,2-雙二苯基膦基乙烷)鈦、氯環戊二烯基(三苯基膦)鈦、氯環戊二烯基(四氫噻吩)鈦、溴環戊二烯基(四氫呋喃)鈦、碘環戊二烯基(四氫呋喃)鈦、氯(甲基環戊二烯基)(四氫呋喃)鈦、氯(1,3-二



## 五、發明說明 (15)

甲基環戊二烯基)(四氫呋喃)鈳、氯(1-丁基-3-甲基環戊二烯基)(四氫呋喃)鈳、氯(四甲基環戊二烯基)(四氫呋喃)鈳、氯(五甲基環戊二烯基)(四氫呋喃)鈳、氯(三甲基甲矽烷基環戊二烯基)(四氫呋喃)鈳、氯(1,2-雙(三甲基甲矽烷基)環戊二烯基)(四氫呋喃)鈳、氯(1,3-雙(三甲基甲矽烷基)環戊二烯基)(四氫呋喃)鈳、氯苊基(四氫呋喃)鈳、氯(2-甲基苊基)(四氫呋喃)鈳、氯(2-三甲基甲矽烷基苊基)(四氫呋喃)鈳、氯芴基(四氫呋喃)鈳、二甲基甲矽烷基(環戊二烯基)(第三丁基胺基)鈳、及二甲基甲矽烷基(四甲基環戊二烯基)(第三丁基胺基)鈳。

由 $R_nMX_{2-n} \cdot L_a$  (其中 $n=2$ )表示之化合物之特定例包括雙環戊二烯基鈳、雙(甲基環戊二烯基)鈳、雙(1,2-二甲基環戊二烯基)鈳、雙(1,3-二甲基環戊二烯基)鈳、雙(1-丁基-3-甲基環戊二烯基)鈳、雙(四甲基環戊二烯基)鈳、雙(五甲基環戊二烯基)鈳、雙(乙基環戊二烯基)鈳、雙(正丙基環戊二烯基)鈳、雙(異丙基環戊二烯基)鈳、雙(正丁基環戊二烯基)鈳、雙(異丁基環戊二烯基)鈳、雙(第二丁基環戊二烯基)鈳、雙(第三丁基環戊二烯基)鈳、雙(1-甲氧基乙基環戊二烯基)鈳、雙(1-二甲基胺基乙基環戊二烯基)鈳、雙(1-二乙基胺基乙基環戊二烯基)鈳、雙(三甲基甲矽烷基環戊二烯基)鈳、雙(1-二甲基膦乙基環戊二烯基)鈳、雙(1,2-雙(三甲基甲矽烷基)環戊二烯基)鈳、雙(1,3-雙(三甲基甲矽烷基)環戊二烯基)鈳、苊基環戊二烯鈳、(2-甲基苊基)環戊二烯鈳、(2-三甲基甲矽烷基苊基)



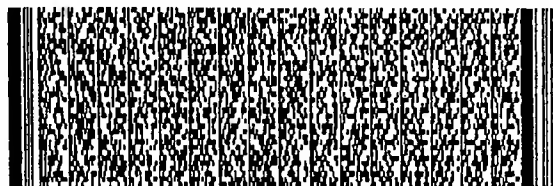
## 五、發明說明 (16)

環戊二烯鈳、雙茛基鈳、雙苄基鈳、茛基苄基鈳、環戊二烯基苄基鈳、二甲基甲矽烷基(環戊二烯基)(第三丁基胺基)鈳、二甲基甲矽烷基(四甲基環戊二烯基)(第三丁基胺基)鈳、二甲基甲矽烷基雙(環戊二烯基)鈳、二甲基甲矽烷基雙(茛基)鈳及二甲基甲矽烷基雙(苄基)鈳。

由 $R_nMX_{3-n} \cdot L_a$  (其中 $n=1$ )所表示之化合物之特定例包括二氯化化合物如二氯化環戊二烯鈳、二氯化甲基環戊二烯鈳、二氯化(1,3-二甲基環戊二烯基)鈳、二氯化(1-甲基-3-丁基環戊二烯基)鈳、二氯化(五甲基環戊二烯基)鈳、二氯化(三甲基甲矽烷基環戊二烯基)鈳、二氯化(1,3-雙(三甲基甲矽烷基)環戊二烯基)鈳、二氯化茛基鈳、二氯化(2-甲基茛基)鈳、二氯化(2-三甲基甲矽烷基茛基)鈳、及二氯化苄基鈳及藉甲基取代此等化合物中氯原子所得之二甲基化合物。

由 $R_nMX_{3-n} \cdot L_a$ 表示之化合物之其他例包括其中R及X與烴或甲矽烷基互相連接者。此等化合物之例包括氯化醯胺化合物如氯化(第三丁基醯胺)二甲基( $\eta^5$ -環戊二烯基)矽烷鈳及氯化(第三丁基醯胺)二甲基(四甲基 $\eta^5$ -環戊二烯基)矽烷鈳，及藉甲基取代此等化合物中氯原子所得之甲基化合物。

由 $R_nMX_{3-n} \cdot L_a$ 表示之化合物之其他例包括醇鹽化合物如二甲氧化環戊二烯鈳、環戊二烯鈳二(異丙氧化物)、環戊二烯鈳二(第三丁氧化物)、二苯氧化環戊二烯鈳、甲氧氯化環戊二烯鈳、異丙氧氯化環戊二烯鈳、第三丁氧氯化環



## 五、發明說明 (17)

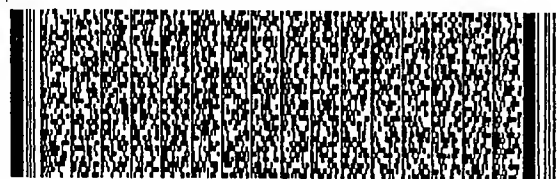
戊二烯鈳及苯氧氯化環戊二烯鈳及藉甲基取代此等化合物中氯原子所得之甲基化化合物。

由 $R_nMX_{3-n} \cdot L_a$ 表示之化合物之其他例包括雙醯胺化合物如(環戊二烯基)(雙二乙醯胺)鈳、(環戊二烯基)(雙(二-異丙基醯胺))鈳及(環戊二烯基)(雙(二-正辛基醯胺))鈳。

由 $R_nMX_{3-n} \cdot L_a$ 表示之化合物之其他例包括磷錯合物如二氯化環戊二烯鈳、雙三乙基磷錯合物、二氯化環戊二烯鈳、雙三甲基磷錯合物、(環戊二烯基)(雙(二-異丙基醯胺))鈳三甲基磷錯合物及二氯化單甲基環戊二烯鈳雙三乙基磷錯合物。

由 $R_nMX_{3-n} \cdot L_a$ (其中 $n=2$ )表示之化合物之例包括氯化化合物如氯化二環戊二烯鈳、氯化雙(甲基環戊二烯基)鈳、氯化雙(1,3-二甲基環戊二烯基)鈳、氯化雙(1-丁基-3-甲基環戊二烯基)鈳、氯化雙(五甲基環戊二烯基)鈳、氯化雙(三甲基甲矽烷基環戊二烯基)鈳、氯化雙(1,3-雙(三甲基甲矽烷基)環戊二烯基)鈳、氯化二茛基鈳、氯化雙(2-甲基茛基)鈳、氯化雙(2-三甲基甲矽烷基茛基)鈳及氯化二芴基鈳及藉甲基取代此等化合物中氯原子所得之甲基化化合物。

由 $R_nMX_{3-n} \cdot L_a$ (其中 $n=2$ )表示之化合物之其他例包括甲氧化二環戊二烯鈳、異丙氧化二環戊二烯鈳、第三丁氧化二環戊二烯鈳、苯氧化二環戊二烯鈳、二環戊二烯基(二乙醯胺)鈳、二環戊二烯基(二-異丙醯胺)鈳及二環戊二烯基



## 五、發明說明 (18)

(二-正辛醯胺)鈦。

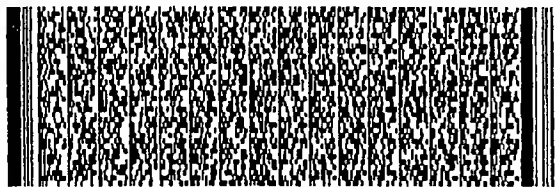
由  $R_nMX_{3-n} \cdot L_a$  (其中  $n=2$ ) 表示之化合物之其他例包括其中 R 與烴或甲矽烷基互相連接者。此等化合物之例包括氯化化合物如氯化二甲基 ( $\eta^5$ -環戊二烯基) 矽烷鈦及氯化二甲基雙 (四甲基- $\eta^5$ -環戊二烯基) 矽烷鈦，及藉甲基取代此等化合物中氯原子所得之甲基化化合物。

由  $RM(O)X_2$  表示之化合物之特定例包括二氯化環戊二烯氧鈦、二氯化甲基環戊二烯氧鈦、二氯化 (1,3-二甲基環戊二烯基) 氧鈦、二氯化 (1-丁基-3-甲基環戊二烯基) 氧鈦、二氯化 (五甲基環戊二烯基) 氧鈦、二氯化 (三甲基甲矽烷基環戊二烯基) 氧鈦、二氯化 (1,3-雙 (三甲基甲矽烷基) 環戊二烯基) 氧鈦、二氯化茚基氧鈦、二氯化 (2-甲基茚基) 氧鈦、二氯化 (2-三甲基甲矽烷基茚基) 氧鈦及二氯化芴基氧鈦。

由  $RM(O)X_2$  表示之化合物之其他例包括藉甲基取代前述化合物中氯原子所得之二甲基化化合物。

由  $RM(O)X_2$  表示之化合物之其他例包括其中 R 及 X 與烴或甲矽烷基互相連接者。此等化合物之例包括氯化醯胺化合物如氯化 (第三丁基醯胺) 二甲基 ( $\eta^5$ -環戊二烯基) 矽烷氧鈦及氯化 (第三丁基醯胺) 二甲基 (四甲基- $\eta^5$ -環戊二烯基) 矽烷氧鈦，及藉甲基取代此等化合物中氯原子所得之甲基化化合物。

此等化合物之其他例包括二甲氧化環戊二烯氧鈦、環戊二烯氧鈦二 (異丙氧化物)、環戊二烯氧鈦二 (第三丁氧化



## 五、發明說明 (19)

物)、二苯氧化環戊二烯氧鈦、甲氧氯化環戊二烯氧鈦、異丙氧氯化環戊二烯氧鈦、第三丁氧氯化環戊二烯氧鈦，及苯氧氯化環戊二烯氧鈦。

此等化合物之其他例包括藉甲基取代前述各種化合物中氯原子所得之甲基化化合物。

此等化合物之例包括(環戊二烯基)(雙二乙醯胺)氧鈦、(環戊二烯基)(雙二異丙醯胺)氧鈦，及(環戊二烯基)(雙二-正辛醯胺)氧鈦。

由 $R_nMX_{3-n}(NR')$ 表示之化合物之特定例包括二氧化環戊二烯基(甲基亞胺)鈦、二氯化環戊二烯基(苯基亞胺)鈦、二氯化環戊二烯基(2,6-二甲基苯基亞胺)鈦、二氯化環戊二烯基(2,6-二-異丙基苯基亞胺)鈦、二氯化(甲基環戊二烯基)(苯基亞胺)鈦、二氯化(1,3-二甲基環戊二烯基)(苯基亞胺)鈦、二氯化(1-丁基-3-甲基環戊二烯基)(苯基亞胺)鈦、二氯化(五甲基環戊二烯基)(苯基亞胺)鈦、二氯化茚基(苯基亞胺)鈦、二氯化2-甲基茚基(苯基亞胺)鈦，及二氯化芴基(苯基亞胺)鈦。

由 $R_nMX_{3-n}(NR')$ 表示之化合物之其他例包括其中R及X與烴或甲矽烷基互相連接者。此等化合物之例包括氯化醯胺化合物如氯化(第三丁基醯胺)二甲基( $\eta^5$ -環戊二烯基)矽烷(苯基亞胺)鈦及氯化(第三丁基醯胺)二甲基(四甲基- $\eta^5$ -環戊二烯基)矽烷(苯基亞胺)鈦，及藉甲基取代此等化合物中氯原子所得之甲基化化合物。

由 $R_nMX_{3-n}(NR')$ 表示之化合物之其他例包括其中R'與烴或





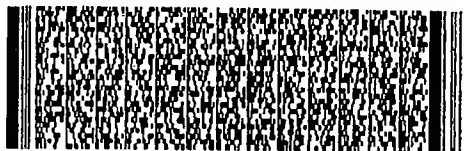
## 五、發明說明 (20)

甲矽烷基互相連接者。此等化合物之例包括氯化亞胺化合物如氯化二甲基雙( $\eta^5$ -環戊二烯基)矽烷(苯基亞胺)鈦、氯化二甲基雙( $\eta^5$ -環戊二烯基)矽烷(甲苯亞胺)鈦、氯化二甲基雙(四甲基- $\eta^5$ -環戊二烯基)矽烷(苯基亞胺)鈦及氯化二甲基(四甲基- $\eta^5$ -環戊二烯基)矽烷(甲苯亞胺)鈦，及藉甲基取代此等化合物中氯原子所得之甲基化化合物。

此等化合物之其他例包括二甲氧化環戊二烯鈦(苯基亞胺)、二-異丙氧化環戊二烯鈦、氯化環戊二烯鈦(苯基亞胺)(異丙氧基)、(環戊二烯基)(雙二乙醯胺)鈦(苯基亞胺)、及(環戊二烯基)(雙-異丙醯胺)鈦(苯基亞胺)。

在本發明之成份(B)中構成由非配位陰離子與陽離子所製成之離子化合物之非配位陰離子之例包括四(苯基)硼酸鹽、四(氟苯基)硼酸鹽、四個(二氟苯基)硼酸鹽、四個(三氟苯基)硼酸鹽、四個(四氟苯基)硼酸鹽、四個(五氟苯基)硼酸鹽、四個(四氟甲基苯基)硼酸鹽、四個(3,5-雙三氟甲基苯基)硼酸鹽、四個(甲苯基)硼酸鹽、四個(二甲苯基)硼酸鹽、三苯基(五氟苯基)硼酸鹽、三(五氟苯基)(苯基)硼酸鹽、三十氫化物-7,8-二卡巴十二硼酸鹽、四氟硼酸鹽及六氟磷酸鹽。

另一方面，在本發明成份(B)中構成由非配位陰離子與陽離子所製成之離子化合物之陽離子之例包括碳鎢陽離子、氧鎢陽離子、鉍陽離子、鎘陽離子、環庚三烯陽離子及鈾鐵陽離子含有過渡金屬。



## 五、發明說明 (21)

碳鎔陽離子之特定例包括三取代之碳鎔陽離子如三苯基碳鎔陽離子及三取代之苯基碳鎔陽離子。三取代之苯基碳鎔陽離子之特定例包括三(甲基苯基)碳鎔陽離子及三個(二甲基苯基)碳鎔陽離子。

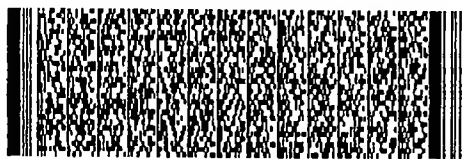
銨陽離子之特定例包括三烷基銨陽離子如三甲基銨陽離子、三乙基銨陽離子、三丙基銨陽離子、三(異丁基)銨陽離子及三(正丁基)銨陽離子、N,N-二烷基苯胺鎔陽離子如N,N-二甲基苯胺鎔陽離子、N,N-二乙基苯胺鎔陽離子及N,N-2,4,6-三甲基苯胺鎔陽離子及二烷基銨陽離子如二(異丙基)銨陽離子及二環己基銨陽離子。鎘陽離子之特定例包括三芳基鎘陽離子如三苯鎘陽離子、三(甲基苯基)鎘陽離子及三個(二甲基苯基)鎘陽離子。

關於前述離子化合物，較好使用組合成份包含視需要選自前述非配位陰離子與陽離子所組成族群者。

離子化合物之較佳例包括三苯碳鎔四個(五氟苯基)硼酸鹽，三苯碳鎔四個(3,5-雙三氟甲基苯基)硼酸鹽，三苯碳鎔四個(氟苯基)硼酸鹽，N,N-二甲基苯胺碳鎔四個(五氟苯基)硼酸鹽，N,N-二甲基苯胺鎔四個(3,5-雙三氟甲基苯基)硼酸鹽，及1,1'-二甲基銻鐵四個(五氟苯基)硼酸鹽。

此等離子化合物可以單獨或其二種以上之組合方式使用。

作為本發明之成份(C)之週期表I至III族元素之有機金屬化合物之例包括有機鋁化合物、有機鋰化合物、有機鎂化合物、有機鋅化合物及有機硼化合物。成份(C)之加入



## 五、發明說明 (22)

可產生增加聚合活性之效果。

此等有機金屬化合物之特定例包括甲基鋰、丁基鋰、苯基鋰、苄基鋰、新戊基鋰、三甲基甲矽烷基鋰、雙三甲基甲矽烷基甲基鋰、二丁基鎂、二己基鎂、二乙基鎂、二甲基鋅、三甲基鋁、三乙基鋁、三異丁基鋁、三己基鋁、三辛基鋁、三癸基鋁、三氯化硼及三苯基硼。

此等有機金屬化合物之其他例包括有機金屬鹵化物如氯化乙基鎂、氯化丁基鎂、氯化二甲基鋁、氯化二乙基鋁、氯化倍半乙基鋁及二氯化乙基鋁，及氫化有機金屬化合物如氫化二乙基鋁及氫化倍半乙基鋁。

作為本發明成份(C)之週期表I至III族元素之有機金屬化合物中較佳者為有機鋁化合物。

作為本發明成份(C)之有機鋁化合物之特定例包括三烷基鋁如三甲基鋁、三乙基鋁及三異丁基鋁、有機鋁鹵化物如氯化二甲基鋁、氯化二乙基鋁、氯化倍半乙基鋁及二氯化乙基鋁及氫化有機鋁化合物如氫化二乙基鋁及氫化倍半乙基鋁。

關於成份(C)，亦可使用鋁矜烷。關於該鋁矜烷，可使用由有機鋁化合物與縮合劑互相接觸所得者。鋁矜烷之例包括由通式 $(-Al(R')O-)_n$ 表示之鏈鋁矜烷，及環狀鋁矜烷，其中 $R'$ 表示 $C_{1-10}$ 烴基，其可藉鹵原子及/或烷氧基局部取代，詞尾 $n$ 表示不低於5，較佳為不低於10之聚合度。由 $R'$ 表示之 $C_{1-10}$ 烴基之例包括甲基、乙基、丙基及異丁基。在此等 $C_{1-10}$ 烴基中較佳者為甲基及乙基。鋁矜烷之粗料之



## 五、發明說明 (23)

例包括三烷基鋁如三甲基鋁、三乙基鋁及三異丁基鋁及其混合物。三甲基鋁與三丁基鋁之混合物。三甲基鋁與三丁基鋁之混合物作為鋁噶烷之粗料較佳。

前述有機鋁化合物可單獨或以其二種或以上之組合使用。

作為成份(A)之金屬茂型錯合物對作為成份(B)之離子化合物之莫耳比較佳為1:0.1至1:10，更佳為1:0.2至1:5。

作為成份(A)之金屬茂型錯合物對作為成份(C)之週期表I至III族元素之有機金屬化合物之莫耳比較佳為1:0.1至1:1000，更佳為1:10至1:1000，特佳為1:10至1:500。

作為成份(C)之有機金屬化合物對作為成份(D)之水之莫耳比較佳為0.66至5，更佳為0.7至1.5特佳為0.8至1.5。

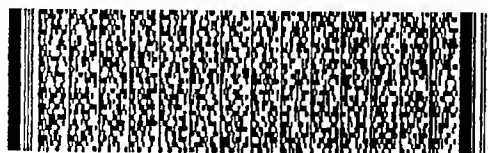
觸媒成份之加入順序不受特定限制。但實際上，觸媒成份可以下面順序加入。

1) 將成份(D)加入欲聚合之共軛二烯化合物單體或單體與溶劑之混合物中。然後，將成份(C)加入混合物中。然後以任意順序將成份(A)與成份(B)加入混合物中。

2) 將成份(D)與成份(C)加入欲聚合之共軛二烯化合物單體或單體與溶劑之混合物中。然後以任意順序將成份(A)與成份(B)加入混合物中。

在前述程序中，欲聚合之共軛二烯化合物單體可完全或部份加入。若欲聚合之共軛二烯化合物單體部份加入時，前述接觸混合物可與其餘單體或其餘單體之溶液混合。

共軛二烯化合物單體之例包括1,3-丁二烯、異丙烯、1,



## 五、發明說明 (24)

3-戊二烯、2-乙基-1,3-丁二烯、2,3-二甲基丁二烯、2-甲基戊二烯、4-甲基戊二烯及2,4-己二烯。

二種或以上此等共軛二烯化合物單體可組合使用。

單體成份可包含環狀單烯烴如乙烯、丙烯、丁烯-1、丁烯-2、異丁烯、戊烯-1、4-甲基戊烯-1、己烯-1及辛烯-1，環狀單烯烴如環戊烯、環己烯及降冰片烯及/或芳香乙烯化合物如苯乙烯及 $\alpha$ -甲基苯乙烯及非共軛二烯烴如二環戊二烯、5-伸乙烯-2-降冰片烯及1,5-己二烯(小量)。

此處可用之聚合法不受特殊限制。例如，可使用本體聚合、溶液聚合等。溶液聚合所用之溶劑之例包括芳香烴如甲苯、苯及二甲苯，脂肪烴如正己烷、丁烷、庚烷及戊烷，脂環族烴如環戊烷及環己烷，烯烴如1-丁烯、順式-2-丁烯及反式-2-丁烯，烴溶劑如礦物精、溶劑石腦油及石油，及氫化烴溶劑如二氯甲烷。1,3-丁二烯本身可用作聚合溶劑。

在本發明中，即使有，使用共軛二烯作為聚合溶劑本身之本體聚合之優點在於不需大量能量回收溶劑。

若溶液聚合用於本發明時，以甲苯、環己烷、順式-2-丁烯與反式-2-丁烯之混合物等用作溶劑較佳。

在本發明中，共軛二烯化合物可在修改產物分子量之前述觸媒及氫存在下聚合。

欲呈現於聚合之氫量，基於1莫耳所用共軛二烯，較佳為不超過500毫莫耳或不超過12升在20℃及1 atm.，更佳



## 五、發明說明 (25)

為不超過50毫莫耳或不超過1.2升在20℃及1 atm.，特佳為0.005至20毫莫耳或0.0001至0.48升在20℃及1 atm.。

氫可被連續導入聚合槽內。

聚合溫度較佳為-100℃至120℃，更佳為-50℃至120℃，特佳為-50℃至100℃，聚合時間較佳為2分鐘至12小時，更佳為10分鐘至12小時，再佳為10分鐘至6小時，特佳為30分鐘至6小時。

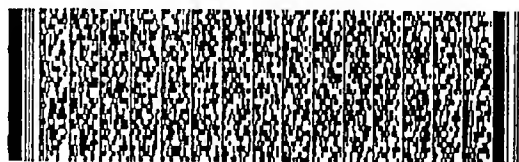
欲聚合之物料實施聚合一段預定時間。必要時，停止物如醇再加入以終止聚合。必要時，聚合槽中之壓力被釋放。然後將產物實施後處理如洗滌及乾燥。

本發明聚合法之用途可產生一種具有1,2-結構含量為4至30%，較佳為5至25%，更佳為5至20%，特佳為7至15%，順式-1,4-結構含量為65至95%，較佳為70至95%，更佳為70至92%及反式-1,4-結構含量為不超過5%，較佳為不超過4.5%，特佳為0.5至4.0%之聚丁二烯。

若微觀結構在上述界定之範圍以外時，所得聚合物留下一些東西在反應性方面有用(接枝反應性或交聯反應性)。若用作添加劑時，聚合物提供不良橡膠性，不利影響物性與外觀之平衡。

根據本發明之聚合法，具有在30℃甲苯中所測定之固有黏度 $[\eta]$ 為0.1至20之聚丁二烯可產生。

另外，本發明聚合法之用途可產生一種具有以聚苯乙烯作為標準物質藉GPC測定之重量平均分子量為10,000至4,000,000之聚丁二烯。



## 五、發明說明 (26)

根據本發明所製成之聚丁二烯顯示 $T_{cp}/ML_{1+4}$ 比為2至6，較佳為2.5至5，其中在 $100^{\circ}\text{C}$ 下 $T_{cp}$ 為甲苯溶液黏度， $ML_{1+4}$ 為門尼黏度。

本發明聚丁二烯之甲苯溶液黏度( $T_{cp}$ )為20至500，較佳為30至350。

本發明聚丁二烯之門尼黏度( $ML_{1+4}$ )為10至200，較佳為20至100。

本發明聚丁二烯之分子量，根據在 $30^{\circ}\text{C}$ 甲苯中測定之固有黏度( $\eta$ )計算為0.1至10，較佳為0.1至5。

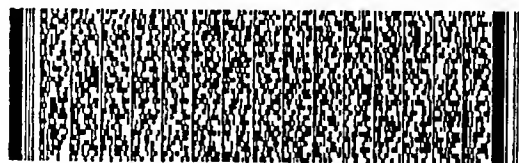
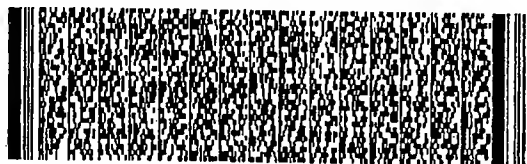
此等聚丁二烯較佳可用作聚苯乙烯之衝擊改質劑。

欲聚合之單體較好在聚合前在 $40^{\circ}\text{C}$ 下與前述觸媒成份接觸1至60分鐘。換言之，欲聚合之單體較好在預定溫度下在前述觸媒存在下實施預聚合，本發明之預聚合可藉氣相法、漿液法、本體法等完成。預聚合法所得之固體物質可在後續聚合前分離或不分離。

聚合時間通常不超過600分鐘，較佳為不超過120分鐘，更佳為30秒至120分鐘。若預聚合時間超出上述界定範圍以外時，其缺點是後續聚合在不足活性下實施。

預聚合後在不高於 $40^{\circ}\text{C}$ ，較佳為 $-100^{\circ}\text{C}$ 至 $40^{\circ}\text{C}$ ，更佳為 $-50^{\circ}\text{C}$ 至 $40^{\circ}\text{C}$ 下於各種觸媒成份存在下實施。若預聚合溫度超出上述界定範圍以外時，後續聚合會在相當低活性下實施。此外，聚合在預聚合時進行太遠，造成程序問題。

在預聚合時，氫必要時可存在。欲存在於聚合之氫量較佳為基於1莫耳所用之共軛二烯，在 $20^{\circ}\text{C}$ 及1 atm. 下不超



## 五、發明說明 (27)

過500毫莫耳或不超過12升，特別是在20℃及1 atm. 下0.005至20毫莫耳或0.0001至0.48升。

本發明進一步以下列實例說明，但不受其所限制。

聚丁二烯之微觀結構係藉紅外線吸收光譜分析。詳言之，聚丁二烯之微觀結構對順式-1,4-結構在740  $\text{cm}^{-1}$ ，對反式-1,4-結構在967  $\text{cm}^{-1}$ 及對1,2-結構在911  $\text{cm}^{-1}$ 下自吸收強度之比計算(乙烯基)。

關於分子量分佈之評估，測定 $M_w/M_n$ 之比，其中 $M_w$ 為用聚苯乙烯作為標準物質藉GPC測定之重量平均分子量， $M_n$ 為數目平均分子量。

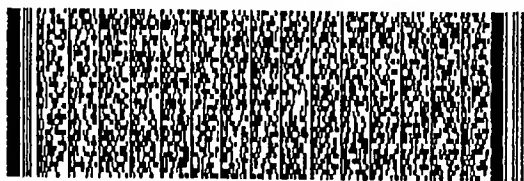
聚丁二烯之固有黏度 $[\eta]$ 係在30℃下於甲苯溶液中測定。

聚合物之門尼黏度( $ML_{1+4}$ )係根據JIS K 6300測定。

聚合物之甲苯溶液黏度( $T_{cp}$ )係藉溶解2.28 g聚合物於50 ml 甲苯中，並在25℃下根據JIS Z 8809使用黏度計移正標準液體藉Canon Fenske黏度計No. 400將聚合物之甲苯溶液實施黏度測定而測定。

## 實例1至14

將400 ml (248 g)1,3-丁二烯裝入1.5升熱壓器內(其中之空氣由氬氣取代)。然後攪動物質。然後將水( $\text{H}_2\text{O}$ )加入物質中，如表1所示。將混合物攪拌30分鐘作成溶液。隨後，以在20℃及1 atm. 下藉整合質量流動計測定之200 ml之量將氬氣導入熱壓器內。接著，以表1所示之量將三乙基鋁(1毫莫耳/ml 甲苯溶液)加入混合物中。3分鐘後，將





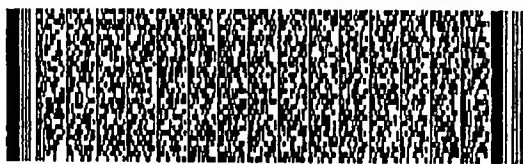
## 五、發明說明 (28)

0.8 ml 三氯化環戊二烯鈦( $\text{CpVCl}_3$ )(0.005毫莫耳/ml 甲苯溶液)加入混合物中。然後將4 ml 三苯碳鎢四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025毫莫耳/ml 甲苯溶液)加入混合物中。然後混合物在40 °C下實施聚合一段時間,如表1所示。

聚合後,將等份含有微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。然後將熱壓器之壓力釋放。將產物澆入乙醇中以沉澱聚合物,然後其後藉過濾收回及乾燥。聚合之結果示於表2及3。

表1

實例號數	$\text{H}_2\text{O}$ (D)	TEA (C)	$\text{TEA}/\text{H}_2\text{O}$ (C)/(D)	聚合時間
	(毫莫耳)	(毫莫耳)		(分鐘)
1	0.12	0.28	2.33	30
2	0.12	0.3	2.50	30
3	0.12	0.34	2.83	30
4	0.12	0.36	3.00	30
5	0.29	0.46	1.59	30
6	0.29	0.48	1.66	25
7	0.29	0.5	1.72	30
8	0.29	0.54	1.86	30
9	0.4	0.6	1.50	25
10	0.4	0.66	1.65	30
11	0.4	0.74	1.85	30
12	0.68	0.82	1.21	30
13	0.68	0.84	1.24	30
14	0.68	0.86	1.26	30



## 五、發明說明 (29)

表 2

實例號數	產率	聚合活性
	(g)	(g/毫莫耳.V.h.)
1	37.8	18,900
2	62.9	31,450
3	50.1	25,050
4	33.0	16,500
5	24.0	12,000
6	75.9	45,540
7	53.6	26,800
8	44.5	22,250
9	74.7	44,820
10	69.4	34,700
11	59.5	29,750
12	46.1	23,050
13	64.5	32,250
14	58.5	29,250



## 五、發明說明 (30)

表 3

實例號數	[ $\eta$ ]	微觀結構(%)		
		順式	反式	1,2-
1	2.05	88.0	0.8	11.2
2	2.23	88.1	0.8	11.1
3	2.03	88.0	0.8	11.2
4	1.70	88.1	0.7	11.2
5	2.12	88.1	0.7	11.2
6	2.51	87.8	0.8	11.4
7	2.00	88.0	0.8	11.2
8	1.80	88.0	0.8	11.2
9	2.46	88.6	0.6	10.8
10	2.24	88.6	0.6	10.8
11	2.10	88.4	0.8	10.8
12	2.00	88.2	0.6	11.2
13	2.21	88.0	0.6	11.4
14	2.15	87.8	0.8	11.4



## 五、發明說明 (31)

## 實例15至18

將300 ml 甲苯、400 ml 順式-2-丁烯及300 ml (186 g) 1,3-丁二烯裝入1.5升熱壓器內(其中之空氣由氮氣取代)。然後攪動混合物。然後將水( $H_2O$ )加入混合物中,如表4所示。將混合物攪拌30分鐘作成溶液。隨後,以在20°C及1 atm.下藉整合質量流動計測定之130 ml之量將氮氣導入熱壓器內。接著,以表4所示之量將三乙基鋁(1毫莫耳/ml 甲苯溶液)加入混合物中。3分鐘後,將1.6 ml 環戊二烯基(苯)鈮( $CpV(C_6H_5)$ )(0.005毫莫耳/ml 甲苯溶液)加入混合物中。然後將6.4 ml 三苯碳鎢四個(五氟苯基)硼酸鹽( $Ph_3CB(C_6F_5)_4$ )(0.0025毫莫耳/ml 甲苯溶液)加入混合物中。然後混合物在60°C下實施聚合30分鐘。

聚合後,將等份含有微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。然後將熱壓器之壓力釋放。將產物澆入乙醇中以沉澱聚合物,然後其後藉過濾收回及乾燥。聚合之結果示於表5及6。

表4

實例號數	H <sub>2</sub> O (D)	TEA (C)	TEA/H <sub>2</sub> O (C)/(D)	聚合時間 (分鐘)
	(毫莫耳)	(毫莫耳)		
15	1.0	2.0	2.0	30
16	1.3	2.0	1.5	30
17	1.6	2.0	1.3	30
18	1.5	3.0	2.0	30

## 五、發明說明 (32)

表 5

實例號數	產率
	(g)
15	52.5
16	46.7
17	38.4
18	47.9

表 6

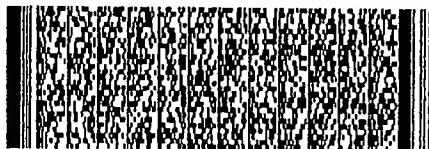
實例號數	[ $\eta$ ]	微觀結構(%)		
		順式	反式	1,2-
15	1.62	87.9	1.4	10.7
16	1.54	88.0	1.3	10.7
17	1.38	87.7	1.4	10.9
18	1.52	88.0	1.3	10.7

參考例 1 至 5

首先，1.5 升熱壓器中之水含量(以下稱為"基本水含量")係根據下列程序測定。

測定程序

藉由分子篩將 1.0 升 1,3-丁二烯裝入 1.5 升熱壓器內(其中空氣被氮氣所取代)。然後攪拌物料。接著將水加入表 7



## 五、發明說明 (33)

所示之物料中。然後將混合物攪拌30分鐘作成溶液。然後利用Karl Fischer溫度計測定溶液之水含量。丁二烯中水含量之結果示於表7。

以全部五次加入之不同水量實施上述所用之相同程序。然後從前述丁二烯中水含量與五次加入之平均水量間之差異計算基本水含量。結果基本水含量為4 mg。依照此值來計算下列實例中之TEA/H<sub>2</sub>O比率。

實例19至23

將1.0升1,3-丁二烯藉由分子篩裝入1.5升熱壓器內(其中之空氣由氮氣取代)。然後攪動物料。然後將水加入物料中,如表8所示。將混合物攪拌30分鐘作成溶液。隨後,以在20℃及1 atm.下藉整合質量流動計測定之200 ml之量將氮氣導入丁二烯內。接著,以表8所示之量將三乙基鋁(1毫莫耳/ml甲苯溶液)加入混合物中。攪拌10分鐘後,將2.5 ml三氯化環戊二烯鈦(CpVCl<sub>3</sub>)(0.005毫莫耳/ml甲苯溶液)及10 ml三苯基碳鎢四個(五氟苯基)(Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>)硼酸鹽(0.0025毫莫耳/ml甲苯溶液)按序加入混合物中。如表9所示。然後混合物在40℃下實施聚合30分鐘。

聚合後,將等份含有微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。然後將熱壓器之壓力釋放。將產物澆入乙醇中以沉澱聚合物,然後其後藉過濾收回及乾燥。聚合之結果示於表9及10。

實例24至28

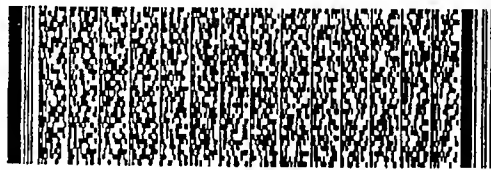
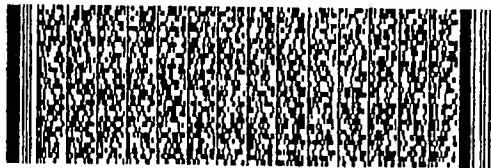
## 五、發明說明 (34)

將1.0升1,3-丁二烯藉由分子篩裝入1.5升熱壓器內(其中之空氣由氬氣取代)。然後攪動物料。隨後,以在20℃及1 atm.下藉整合質量流動計測定之200 ml之量將氬氣導入丁二烯內。接著,以表8所示之量將三乙基鋁(1毫莫耳/ml 甲苯溶液)加入混合物中。然後將混合物攪拌10分鐘。然後,以表8所示之量將水加入混合物並攪拌。攪拌30分鐘後,將2.5 ml 三氯化環戊二烯鈦( $\text{CpVC1}_3$ )(0.005毫莫耳/ml 甲苯溶液)及10 ml 三苯基碳鎢四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025毫莫耳/ml 甲苯溶液)按序加入混合物中,如表8所示。然後混合物在40℃下實施聚合30分鐘。

聚合後,將等份含微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。然後將熱壓器內壓力釋放。將產物澆入乙醇中以沉澱聚合物,然後其藉過濾收回並乾燥。聚合之結果示於表9及10。

比較例1至2

依照實例19至23之程序可得1升具有控制1,3-丁二烯含量之1,3-丁二烯。以在20℃及1 atm.下藉整合質量流動計測定之200 ml之量將氬氣導入1,3-丁二烯內。接著,將2.5 ml 三氯化環戊二烯鈦( $\text{CpVC1}_3$ )(0.005毫莫耳/ml 甲苯溶液)及10 ml 三苯基碳鎢四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025毫莫耳/ml 甲苯溶液)按序加入混合物中,如表9所述。然後,以表8所示之量將三乙基鋁(1毫莫耳/ml 甲苯溶液)加入混合物中。攪拌10分鐘後,混合物



## 五、發明說明 (35)

在40℃下實施聚合30分鐘。

聚合後，將等份含微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。然後將熱壓器內壓力釋放。將產物澆入乙醇中以沉澱聚合物，然後其藉過濾收回並乾燥。聚合之結果示於表9及10。

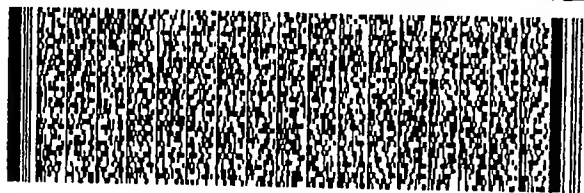
## 比較例3至4

除了以表8所示之量加入三乙基鋁(1毫莫耳/ml甲苯溶液)以外，依照實例24至28之程序。攪拌10分鐘後，將2.5 ml 三氯化環戊二烯鈦( $\text{CpVCl}_3$ )(0.005毫莫耳/ml甲苯溶液)及10 ml 三苯基碳鎗四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025毫莫耳/ml甲苯溶液)按序加入混合物中，如表9所示。然後將水加入混合物與攪拌，如表8所示。攪拌10分鐘後，混合物在40℃下實施聚合30分鐘。

聚合後，將等份含小量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物。將熱壓器內壓力釋放。將產物澆入乙醇以沉澱聚合物，其藉過濾收回及乾燥。聚合之結果示於表9及10。

表7

參考例號數	$\text{H}_2\text{O}$		
	加入之水	丁二烯中之水含量	基本水含量
	(mg)	(ppm)	(mg)
1	10	14	4
2	20	25	5
3	30	34	4
4	40	43	3
5	50	54	4





## 五、發明說明 (36)

表 8

實例號數	加入 之水	丁二烯中 之水含量	H <sub>2</sub> O(D)	TEA (C)	TEA/ H <sub>2</sub> O (C)/(D)	聚合時間
	(mg)	(ppm)	(毫莫耳)	(毫莫耳)	丁二烯中之全部含量	
實例 19	26	30	1.66	2	1.20	30
實例 20	36	40	2.22	2	0.90	30
實例 21	20	24	1.33	2	1.50	30
實例 22	14	18	1.00	2	2.00	30
實例 23	36	40	2.22	2	0.90	30
實例 24	26	30	1.66	2	1.20	30
實例 25	36	24	2.22	2	0.90	30
實例 26	20	18	1.33	2	1.50	30
實例 27	14	40	1.00	2	2.00	30
實例 28	36	24	2.22	2	0.90	30
比較例 1	20	24	1.33	2	1.50	30
比較例 2	20	24	1.33	2	1.50	30
比較例 3	20	24	1.33	2	1.50	30
比較例 4	20	24	1.33	2	1.50	30

\* 基本水含量 : 4 mg



## 五、發明說明 (37)

表 9

實例號數	加入之順序	產率(g)
實例 19	(D)→(C)→(A)→(B)	168
實例 20	(D)→(C)→(A)→(B)	134
實例 21	(D)→(C)→(A)→(B)	106
實例 22	(D)→(C)→(A)→(B)	88
實例 23	(D)→(C)→(B)→(A)	121
實例 24	(C)→(D)→(A)→(B)	186
實例 25	(C)→(D)→(A)→(B)	152
實例 26	(C)→(D)→(A)→(B)	118
實例 27	(C)→(D)→(A)→(B)	96
實例 28	(C)→(D)→(B)→(A)	138
比較例 1	(D)→(A)→(B)→(C)	5
比較例 2	(D)→(B)→(A)→(C)	2
比較例 3	(C)→(A)→(B)→(D)	4
比較例 4	(C)→(B)→(A)→(D)	9



## 五、發明說明 (38)

表 10

實例號數	[ $\eta$ ]	微觀結構(%)		
		順式	反式	1,2-
實例 19	2.71	87.6	1.3	11.1
實例 20	2.18	87.7	1.2	11.1
實例 21	1.85	87.7	1.2	10.9
實例 22	1.57	87.4	1.4	11.2
實例 23	1.98	87.5	1.6	10.9
實例 24	2.96	87.2	1.4	11.4
實例 25	2.41	87.7	1.1	11.2
實例 26	1.95	87.8	1.4	10.8
實例 27	1.71	87.5	1.3	11.2
實例 28	2.16	87.8	1.3	10.9
比較例 1	0.7	87.7	1.2	11.1
比較例 2	0.62	-	-	-
比較例 3	0.43	87.4	1.3	11.3
比較例 4	0.52	-	-	-

## 實例 29 至 34 及 比較例 5

1.0 升 1,3-丁二烯藉由分子篩裝入 1.5 升熱壓器(其中之空氣由氮氣取代)。然後攪動物料。隨後,將水加入物料,如表 11 所示。將混合物攪拌 30 分鐘作成溶液。以在 20 °C 及 1 atm. 下藉整合質量流動計測定之 200 ml 之量將氮氣導入混合物中。隨後,以表 11 所示之量,將三乙基鋁(1 毫莫耳/ml 甲苯溶液)加入混合物中。將混合物攪拌 10 分鐘。將 1.6 ml 三氯化環戊二烯鈦( $\text{CpVC}l_3$ )(0.005 毫莫耳/ml 甲苯溶液)及 6.4 ml 三苯基碳鎢四個(五氟苯基)硼酸鹽



## 五、發明說明 (39)

( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025 毫莫耳/ml 甲苯溶液)按序加入混合物，如表12所示。混合物在40℃下實施聚合30分鐘。

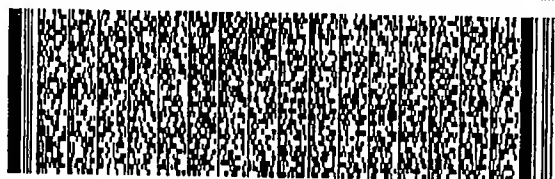
聚合後，將等份含微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。將熱壓器之壓力釋放。將產物澆入乙醇中以沉澱聚合物，然後其藉過濾回收並乾燥。聚合之結果示於表12。

比較例6

除了使用2.5 ml 三氯化環戊二烯鈮( $\text{CpVCl}_3$ )(0.005 毫莫耳/ml 甲苯溶液)及10 ml 三苯基碳鎗四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025 毫莫耳/ml 甲苯溶液)以外，依照比較例5之聚合程序。聚合之結果示於表12。

比較例7

除了使用5 ml 三氯化環戊二烯鈮( $\text{CpVCl}_3$ )(0.005 毫莫耳/ml 甲苯溶液)及20 ml 三苯基碳鎗四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025 毫莫耳/ml 甲苯溶液)以外，依照比較例5之聚合程序。聚合之結果示於表12。



## 五、發明說明 (40)

表 11

實例號數	加入之水	丁二烯中之水含量	H <sub>2</sub> O(D)	TEA (C)	TEA/ H <sub>2</sub> O (C)/(D)	聚合時間
	(mg)	(ppm)	(毫莫耳)	(毫莫耳)	丁二烯中之全部含量	(分鐘)
實例 29	6	10	0.55	0.45	0.81	30
實例 30	6	10	0.55	0.55	0.99	30
實例 31	6	10	0.55	0.65	1.17	30
實例 32	6	10	0.55	0.75	1.35	30
實例 33	6	10	0.55	1.25	2.25	30
實例 34	6	10	0.55	2	3.60	30
比較例 5	6	10	0.55	3.13	5.64	30
比較例 6	6	10	0.55	3.13	5.64	30
比較例 7	6	10	0.55	3.13	5.64	30

\*基本水含量: 4 mg

表 12

實例號數	加入之順序	產率(g)
實例 29	(D)→(C)→(A)→(B)	108
實例 30	(D)→(C)→(A)→(B)	139
實例 31	(D)→(C)→(A)→(B)	155
實例 32	(D)→(C)→(A)→(B)	79
實例 33	(D)→(C)→(B)→(A)	34
實例 34	(D)→(C)→(A)→(B)	19
比較例 5	(D)→(C)→(A)→(B)	6
比較例 6	(D)→(C)→(A)→(B)	28
比較例 7	(D)→(C)→(A)→(B)	88



## 五、發明說明 (41)

參考例6至10

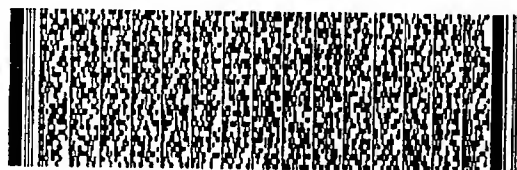
首先，1.5 升熱壓器內之水含量係根據下面程序測定。  
測定程序

1.0 升之300 ml 甲苯、400 ml 順式-2-丁烯與300 ml (184 g) 1,3-丁二烯之溶液藉由分子篩裝入1.5 升熱壓器內(其中之空氣由氮氣所取代)。攪拌混合物。接著，將水加入混合物中，如表13所示。將混合物攪拌30分鐘作成溶液。利用Karl Fischer濕度計測定溶液之水含量。FB(溶劑+丁二烯)中水含量之結果示於表13。

以不同水量全部加入五次實施上述相同程序。從前述FB中之水含量與五次平均之加入水量間之差異來計算基本水含量。結果，基本水含量為4 mg。參照此值來計算下列實例之TEA/H<sub>2</sub>O比。

實例35至37

1.0 升之300 ml 甲苯、400 ml 順式-2-丁烯與300 ml (184 g) 1,3-丁二烯藉由分子篩裝入1.5 升熱壓器(其中之空氣由氮氣所取代)然後攪動物料。隨後，將水加入物料，如表14所示。將混合物攪拌30分鐘作成溶液。以在20 °C 及1 atm. 下藉整合質量流動計測定之130 ml 之量將氮氣導入混合物中。隨後，以表14所示之量，將三乙基鋁(1毫莫耳/ml 甲苯溶液)加入混合物中。在攪拌10分鐘後，將1.6 ml 三氯化環戊二烯鈦(CpVCl<sub>3</sub>)(0.005毫莫耳/ml 甲苯溶液)及6.4 ml 三苯基碳鎢四個(五氟苯基)硼酸鹽(Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>)(0.0025毫莫耳/ml 甲苯溶液)按序加入混合



## 五、發明說明 (42)

物，如表15所示。混合物在60℃下實施聚合30分鐘。

聚合後，將等份含微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。將熱壓器之壓力釋放。將產物澆入乙醇中以沉澱聚合物，然後其藉過濾回收並乾燥。聚合之結果示於表15及16。

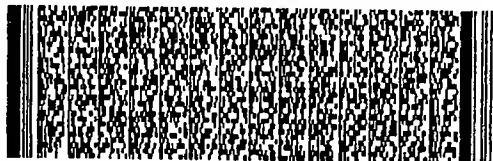
實例38至42

1.0升之300 ml 甲苯、400 ml 順式-2-丁烯與300 ml (184 g) 1,3-丁二烯藉由分子篩裝入1.5升熱壓器(其中之空氣由氬氣所取代)。然後攪動物料。隨後，以在20℃及1 atm. 下藉整合質量流動計測定之130 ml之量將氬氣導入丁二烯中。隨後，以表14所示之量，將三乙基鋁(1毫莫耳/ml 甲苯溶液)加入混合物中。在混合物攪拌10分鐘。以表14所示之量將水加入混合物中並攪拌。在攪拌30分鐘後，將1.6 ml 三氯化環戊二烯鈦( $\text{CpVC1}_3$ )(0.005毫莫耳/ml 甲苯溶液)及6.4 ml 三苯基碳鎗四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025毫莫耳/ml 甲苯溶液)按序加入混合物，如表15所示。混合物在60℃下實施聚合30分鐘。

聚合後，將等份含微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。將熱壓器之壓力釋放。將產物澆入乙醇中以沉澱聚合物，然後其藉過濾回收並乾燥。聚合之結果示於表15及16。

比較例8

1.0升之300 ml 甲苯、400 ml 順式-2-丁烯與300 ml (184 g) 1,3-丁二烯裝入1.5升熱壓器(其中之空氣由氬氣



## 五、發明說明 (43)

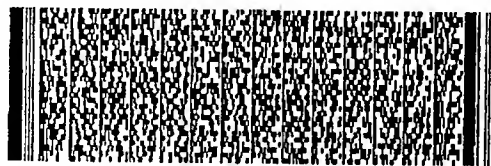
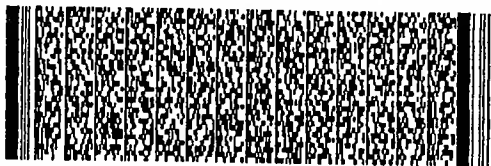
所取代)。然後攪動物料。以在 $20^{\circ}\text{C}$ 及1 atm. 下藉整合質量流動計測定之130 ml之量將氫氣導入熱壓器中。隨後，以表15所示之量，將三乙基鋁(1毫莫耳/ml 甲苯溶液)加入混合物中。將混合物攪拌10分鐘後，將1.6 ml 三氯化環戊二烯鈦( $\text{CpVC1}_3$ )(0.005毫莫耳/ml 甲苯溶液)加入混合物中。然後將6.4 ml 三苯基碳鎢四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025毫莫耳/ml 甲苯溶液)加入混合物。將水加入混合物與攪拌，如表14所示。然後將混合物攪拌30分鐘。混合物在 $60^{\circ}\text{C}$ 下聚合30分鐘。

聚合後，將等份含微量2, 6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。將熱壓器之壓力釋放。將產物澆入乙醇中以沉澱聚合物，然後其藉過濾回收並乾燥。聚合之結果示於表15及16。

比較例9及10

依照實例35至37之程序以得1升具有控制水含量之FB。以在 $20^{\circ}\text{C}$ 及1 atm. 下藉整合質量流動計測定之130 ml之量將氫氣導入FB中。隨後，將1.6 ml 三氯化環戊二烯鈦( $\text{CpVC1}_3$ )(0.005毫莫耳/ml 甲苯溶液)及6.4 ml 三苯基碳鎢四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025毫莫耳/ml 甲苯溶液)按序加入混合物，如表15所示。以表14所示之量將三乙基鋁(1毫莫耳/ml 甲苯溶液)加入混合物中。在攪拌10分鐘後，混合物在 $60^{\circ}\text{C}$ 下實施聚合30分鐘。

聚合後，將等份含微量2, 6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。將熱壓器之壓力釋放。將產





## 五、發明說明 (44)

物澆入乙醇中以沉澱聚合物，然後其藉過濾回收並乾燥。  
聚合之結果示於表15及16。

表 13

參考例號數	H <sub>2</sub> O		
	加入之水 (mg)	FB 中之水含量 (ppm)	基本水含量 (mg)
6	10	14	4
7	20	25	5
8	30	34	4
9	40	43	3
10	50	54	4

表 14

實例號數	H <sub>2</sub> O			TEA (C) 毫莫耳	TEA/ H <sub>2</sub> O (C)/(D) FB 中全部量	聚合時間 (分鐘)
	加入之 水(mg)	FB 中之水 含量(ppm)	毫莫耳			
實例 35	20	24	1.33	2	1.50	30
實例 36	14	18	1.00	2	2.00	30
實例 37	20	24	1.33	2	1.50	30
實例 38	20	24	1.33	2	1.50	30
實例 39	14	18	1.00	2	2.00	30
實例 40	10.4	14.4	0.80	2	2.50	30
實例 41	44	48	2.66	4	1.50	30
實例 42	32	36	2.00	4	2.00	30
比較例 8	20	24	1.33	2	1.50	30
比較例 9	20	24	1.33	2	1.50	30
比較例 10	20	24	1.33	2	1.50	30

\*基本水含量: 4 mg



## 五、發明說明 (45)

表 15

實例號數	加入之順序	產率(g)
實例 35	(D)→(C)→(A)→(B)	90
實例 36	(D)→(C)→(A)→(B)	77
實例 37	(D)→(C)→(B)→(A)	40
實例 38	(C)→(D)→(A)→(B)	110
實例 39	(C)→(D)→(A)→(B)	93
實例 40	(C)→(D)→(A)→(B)	79
實例 41	(C)→(D)→(A)→(B)	75
實例 42	(C)→(D)→(A)→(B)	67
比較例 8	(C)→(A)→(B)→(D)	2
比較例 9	(D)→(B)→(A)→(C)	4
比較例 10	(D)→(A)→(B)→(C)	9

表 16

實例號數	[ $\eta$ ]	微觀結構(%)		
		順式	反式	1,2-
實例 35	2.01	87.4	1.5	11.1
實例 36	1.98	87.7	1.3	11
實例 37	1.24	87.9	1.2	10.9
實例 38	2.89	87.7	1.4	11
實例 39	2.35	87.7	1.3	10.9
實例 40	1.96	87.5	1.4	11.1
實例 41	1.98	87.7	1.3	11
實例 42	1.8	87.8	1.4	10.8
比較例 8	0.74	87.6	1.2	11.2
比較例 9	0.88	87.6	1.1	11.3
比較例 10	0.98	87.3	1.4	11.3



## 五、發明說明 (46)

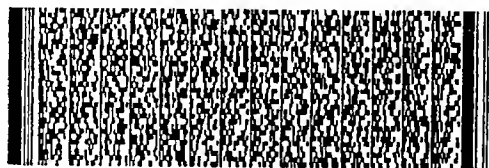
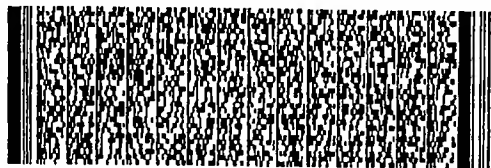
實例43至50及比較例11至14

1.0 升之300 ml 甲苯、400 ml 順式-2-丁烯與300 ml (184 g) 1,3-丁二烯藉由分子篩裝入1.5 升熱壓器(其中之空氣由氮氣所取代)。然後攪動物料。隨後，將水加入物料，如表17 所示。將混合物攪拌30 分鐘。以在20℃及1 atm. 下藉整合質量流動計測定之130 ml 之量將氮氣導入FB(溶劑+丁二烯)中。隨後，以表17 所示之量，將三乙基鋁(1 毫莫耳/ml 甲苯溶液)加入混合物中。將混合物攪拌10 分鐘。在攪拌10 分鐘後，將1.6 ml 三氯化環戊二烯鈦( $\text{CpVCl}_3$ )(0.005 毫莫耳/ml 甲苯溶液)及6.4 ml 三苯基碳鎘四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025 毫莫耳/ml 甲苯溶液)按序加入混合物，如表18 所示。混合物在60℃下實施聚合30 分鐘。

聚合後，將等份含微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。將熱壓器之壓力釋放。將產物澆入乙醇中以沉澱聚合物，然後其藉過濾回收並乾燥。聚合之結果示於表18 及19。

實例51至54及比較例15

1.0 升之300 ml 甲苯、400 ml 順式-2-丁烯與300 ml (184 g) 1,3-丁二烯藉由分子篩裝入1.5 升熱壓器(其中之空氣由氮氣所取代)。然後攪動物料。隨後，以在20℃及1 atm. 下藉整合質量流動計測定之130 ml 之量將氮氣導入物料中。隨後，以表17 所示之量，將三乙基鋁(1 毫莫耳/ml 甲苯溶液)加入混合物中。將混合物攪拌10 分鐘後，在攪



## 五、發明說明 (47)

拌30分鐘後，將1.6 ml 三氯化環戊二烯鈦( $\text{CpVCl}_3$ )(0.005毫莫耳/ml 甲苯溶液)及6.4 ml 三苯基碳鎗四個(五氟苯基)硼酸鹽( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ )(0.0025毫莫耳/ml 甲苯溶液)按序加入混合物，如表18所示。混合物在60℃下實施聚合30分鐘。

聚合後，將等份含微量2,6-二-第三丁基對苯酚之乙醇與庚烷之混合物加入產物中。將熱壓器之壓力釋放。將產物澆入乙醇中以沉澱聚合物，然後其藉過濾回收並乾燥。聚合之結果示於表18及19。



## 五、發明說明 (48)

表 17

實例號數	H <sub>2</sub> O			TEA (C)	TEA/ H <sub>2</sub> O (C)/(D)	聚合時間 (分鐘)
	加入之 水(mg)	FB 中之水 含量(ppm)	毫莫耳	毫莫耳	FB 中之全部量	
實例 43	18	22	1.22	1	0.82	30
實例 44	16	20	1.11	1	0.90	30
實例 45	14	18	1.00	1	1.00	30
實例 46	10	14	0.78	1	1.29	30
實例 47	8	12	0.67	1	1.50	30
實例 48	36	40	2.22	2	0.90	30
實例 49	25	29	1.61	2	1.24	30
實例 50	20	24	1.33	2	1.50	30
實例 51	16	20	1.11	1	0.90	30
實例 52	14	18	1.00	1	1.00	30
實例 53	10	14	0.78	1	1.29	30
實例 54	8	12	0.67	1	1.50	30
比較例 11	4	8	0.44	1	2.25	30
比較例 12	68	72	4.00	2	0.50	30
比較例 13	10.4	14.4	0.80	2	2.50	30
比較例 14	9	13	0.72	2	2.77	30
比較例 15	3.2	7.2	0.40	1	2.50	30

\*基本水含量:4 mg



## 五、發明說明 (49)

表 18

實例號數	加入之順序	產率(g)
實例 43	(D)→(C)→(A)→(B)	89
實例 44	(D)→(C)→(A)→(B)	121
實例 45	(D)→(C)→(A)→(B)	126
實例 46	(D)→(C)→(A)→(B)	107
實例 47	(D)→(C)→(A)→(B)	94
實例 48	(D)→(C)→(A)→(B)	95
實例 49	(D)→(C)→(A)→(B)	101
實例 50	(D)→(C)→(A)→(B)	88
實例 51	(C)→(D)→(A)→(B)	104
實例 52	(C)→(D)→(A)→(B)	135
實例 53	(C)→(D)→(A)→(B)	126
實例 54	(C)→(D)→(A)→(B)	93
比較例 11	(D)→(C)→(A)→(B)	30
比較例 12	(D)→(C)→(A)→(B)	0
比較例 13	(D)→(C)→(A)→(B)	40
比較例 14	(D)→(C)→(A)→(B)	36
比較例 15	(C)→(D)→(A)→(B)	55



## 五、發明說明 (50)

表 19

實例號數	[ $\eta$ ]	微觀結構(%)			ML <sub>1+4</sub>	T <sub>cp</sub>	T <sub>cp</sub> +ML <sub>1+4</sub>
		順式	反式	1,2-			
實例 43	2.22	87.7	1.4	10.9	30	81	2.7
實例 44	3.53	87.8	1.4	10.8			
實例 45	3.59	87.4	1.6	11			
實例 46	2.98	87.8	1.4	10.8	68	320	4.7
實例 47	2.3	87.6	1.3	11.1	34	105	3.1
實例 48	2.46	87.5	1.4	11.1	42	140	3.3
實例 49	2.8	87.5	1.5	11	60	230	3.8
實例 50	1.98	87.7	1.3	11	22	58	2.6
實例 51	2.99	87.5	1.5	11	70	330	4.7
實例 52	3.6	87.6	1.4	11			
實例 53	2.54	87.6	1.3	11.1	43	143	3.3
實例 54	2.32	87.7	1.5	10.8	35	105	3.0
比較例 11	0.68	87.6	1.3	11.1			
比較例 12	-	-	-	-			
比較例 13	1.6	87.6	1.5	10.9			
比較例 14	1.54	87.8	1.4	10.9			
比較例 15	1.88	87.8	1.3	10.9			



## 五、發明說明 (51)

實例55至57

將300 ml 環己烷、400 ml 順式-2-丁烯及300 ml 丁二烯裝入2升熱壓器內(其中之空氣由氮氣取代)。攪拌混合物。接著，將水( $H_2O$ )加入混合物中，如表20所示。將混合物攪拌30分鐘。以在 $20^\circ C$ 及1 atm. 下藉整合質量流動計測定之150 ml之量將氮氣導入混合物內。然後，將2 ml之1.0 莫耳/升三乙基鋁(TEA)之甲苯溶液、1 ml之5毫莫耳/升三氯化環戊二烯鈦( $CpVCl_3$ )之甲苯溶液及4 ml 三苯基碳鎢四個(五氟苯基)硼酸鹽( $Ph_3CB(C_6F_5)_4$ )之甲苯溶液按序加入混合物中。然後混合物在室溫下實施預聚合一段預定時間，如表20所示。之後，將聚合槽加熱至 $60^\circ C$ ，然後實施聚合30分鐘。

聚合後，將含2,6-二-第三丁基對苯酚之乙醇加入反應系統以停止反應。蒸發溶劑以乾燥聚合物。聚合之結果示於表21。

實例58至60

除了同時加入 $CpVCl_3$ 及 $Ph_3CB(C_6F_5)_4$ 以外，依照實例55至57之聚合程序。

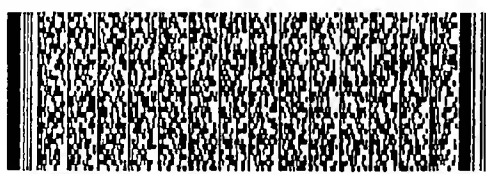
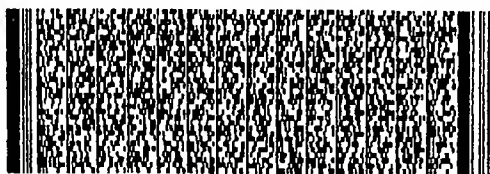
聚合之結果示於表21。

實例61及62

除了按照 $Ph_3CB(C_6F_5)_4$ 及 $CpVCl_3$ 實施觸媒成份之加入以外，依照實例55至57之聚合程序。聚合之結果示於表21。

比較例16及18

除了按照表20所示實施觸媒成份之加入及實施聚合而無





## 五、發明說明 (52)

預聚合以外，依照實例55至62之聚合程序。聚合之結果示於表21。

表 20

實例號數	TEA mmol	H <sub>2</sub> O mmol	TEA/H <sub>2</sub> O	加入之順序	預聚合時間 (分鐘)
實例 55	2	1.33	1.50	水→ TEA → V → B	1
實例 56	2	1.33	1.50	水→ TEA → V → B	5
實例 57	2	1.33	1.50	水→ TEA → V → B	20
實例 58	2	1.33	1.50	水→ TEA → (V,B)	1
實例 59	2	1.33	1.50	水→ TEA → (V,B)	5
實例 60	2	1.33	1.50	水→ TEA → (V,B)	20
實例 61	2	1.33	1.50	水→ TEA → B → V	1
實例 62	2	1.33	1.50	水→ TEA → B → V	5
比較例 16	2	1.33	1.50	水→ TEA → V → B	0
比較例 17	2	1.33	1.50	水→ TEA → (V,B)	0
比較例 18	2	1.33	1.50	水→ TEA → B → V	0



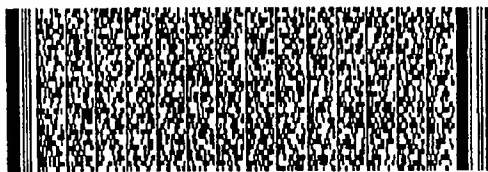
## 五、發明說明 (53)

表 21

實例號數	產率 (g)	[ $\eta$ ]	微觀結構(%)		
			順式	反式	1,2-
實例 55	77	2.07	88.0	1.3	10.7
實例 56	86	2.12	88.0	1.3	10.7
實例 57	75	1.98	88.1	1.2	10.7
實例 58	84	2.13	88.0	1.3	10.7
實例 59	79	2.26	88.0	1.3	10.7
實例 60	65	2.03	88.1	1.3	10.7
實例 61	78	2.00	87.9	1.3	10.8
實例 62	68	1.91	87.9	1.3	10.8
比較例 16	56	1.86	87.9	1.2	10.9
比較例 17	53	1.59	87.7	1.4	10.9
比較例 18	26	1.24	87.9	1.2	10.9

如上所述，本發明提供一種在週期表V族過渡金屬化合物之金屬茂型錯合物存在下，在高聚合活性下製造具有控制微觀結構之共軛二烯聚合物之方法。本發明亦提供一種製造具有含適度加入1,2-結構之高順式結構而在高活性下幾乎無反式結構之微觀結構之聚丁二烯之方法。本發明又提供一種具有含適度加入有1,2-結構之高順式結構而幾乎無反式結構及高直線性之微觀結構之聚丁二烯。

雖然本發明已參照其特殊具體例詳述，熟悉此技藝者當可明白在不脫離本發明之精神及範圍外可對其作各種改變及改良。



## 公告本

案號 87119271

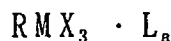
年 月

87年11月12日修正  
補充

## 六、申請專利範圍

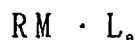
## 1. 一種觸媒，包含：

(A) 週期表V族過渡金屬之金屬茂型錯合物，其為如下通式代表之化合物：



其中R為環戊二烯基，經取代環戊二烯基、茛茛基、茛基或經取代茛基；M為V族過渡金屬之配合物；X為氫原子、鹵原子、C<sub>1-20</sub>烴基、烷氧基或胺基；L為劉易士鹼；a為0，1或2；

或如下通式代表之化合物：



其中R為環戊二烯基，經取代環戊二烯基、茛茛基、茛基或經取代茛基；M為V族過渡金屬之配合物；L為劉易士鹼；a為0，1或2；

(B) 包含非配位陰離子與陽離子之離子化合物，該非配位陰子係選自包括：四(苯基)硼酸鹽、四(氟苯基)硼酸鹽、四(二氟苯基)硼酸鹽、四(三氟苯基)硼酸鹽、四(四氟苯基)硼酸鹽、四(五氟苯基)硼酸鹽、四(四氟甲基苯基)硼酸鹽、四(3,5-雙三氟甲基苯基)硼酸鹽、四(甲苯基)硼酸鹽、四(二甲苯基)硼酸鹽、三苯基(五氟苯基)硼酸鹽、三(五氟苯基)(苯基)硼酸鹽、三十氫化物-7,8-二卡巴十二硼酸鹽、四氟硼酸鹽及六氟磷酸鹽之集團；該非

## 六、申請專利範圍

配位陽離子係選自包括：碳鎢陽離子、氧鎢陽離子、鉍陽離子、磷陽離子、環庚三烯陽離子及含有過渡金屬之銻鐵陽離子之集團；

(C)週期表I-III族元素之有機金屬化合物，

其係選自包括有機鋁化合物、有機鋰化合物、有機鎂化合物、有機鋅化合物及有機硼化合物之集團；

(D)水；

其中(C)/(D)之莫耳比為0.66至5。

2. 根據申請專利範圍第1項之觸媒，其中該週期表V族過渡金屬為釩。

3. 根據申請專利範圍第1項之觸媒，其中該週期表I-III族元素為鋁。

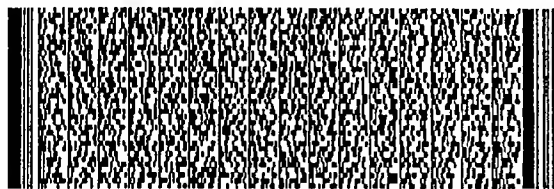
4. 一種製備共軛二烯聚合物之方法，其包括在根據申請專利範圍第1項所定義之觸媒存在下由共軛二烯化合物進行聚合。

5. 根據申請專利範圍第4項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用在氫存在下進行。

6. 根據申請專利範圍第4項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用係進行本體聚合作用。

7. 根據申請專利範圍第4項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用係在作為溶劑之芳香化合物中進行。

8. 根據申請專利範圍第4項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用係在作為溶劑之脂系



## 六、申請專利範圍

化合物中進行。

9. 根據申請專利範圍第4項之製備共軛二烯聚合物之方法，其中共軛二烯化合物之聚合作用係在作為溶劑之2-丁烯中進行。

10. 根據申請專利範圍第4項之製備共軛二烯聚合物之方法，其中該共軛二烯化合物為主要由丁二烯所組成之共軛二烯化合物。

11. 根據申請專利範圍第10項之製備共軛二烯聚合物之方法，其中該週期表I至III族之有機金屬化合物(C)與該水(D)已事先互相接觸。

12. 根據申請專利範圍第10項之製備共軛二烯聚合物之方法，其中該(C)/(D)之莫耳比為0.7至1.5。

13. 根據申請專利範圍第10項之製備共軛二烯聚合物之方法，其中在聚合作用之前，先在不超過40℃之溫度下，與觸媒成份接觸1至60分鐘。

14. 根據申請專利範圍第10項之製備共軛二烯聚合物之方法，其中構成共軛二烯聚合物之丁二烯中1,2-結構單元、順式-1,4-結構單元及反式-1,4-結構單元之含量分別為4至30莫耳%，65至95莫耳%及不超過5莫耳%，且甲苯溶液黏度( $T_{cp}$ )對門尼黏度(Mooney viscosity)在100℃下( $ML_{1+4}$ )之比例( $T_{cp}/ML_{1+4}$ )為2至6。





US006300450B1

(12) **United States Patent**  
Tsujimoto et al.

(10) Patent No.: **US 6,300,450 B1**  
(45) Date of Patent: **Oct. 9, 2001**

(54) **CONJUGATED DIENE COMPOUND  
POLYMERIZATION CATALYST PROCESS  
FOR THE PREPARATION OF CONJUGATED  
DIENE POLYMER IN THE PRESENCE  
THEREOF AND POLYBUTADIENE THUS  
PREPARED**

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(\*) Notice: Subject to any disclaimer, the term of this  
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U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/197,085**

(22) Filed: **Nov. 19, 1998**

(30) **Foreign Application Priority Data**

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Aug. 25, 1998	(JP)	10-238990

(51) Int. Cl.<sup>7</sup> ..... **C08F 36/00**

(52) U.S. Cl. .... **526/335; 526/160; 526/943;  
526/80; 526/91; 526/151; 526/158; 502/152**

(58) Field of Search ..... **502/152; 526/160,  
526/943, 335, 80, 91, 151, 158**

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#### (57) **ABSTRACT**

The present invention provides a process for the production of a conjugated diene polymer having a controlled microstructure at a high polymerization activity in the presence of a metallocene type complex of compound of transition metal of the group V of the Periodic Table. A novel catalyst is provided comprising (A) a metallocene type complex of a transition metal of the group V of the Periodic Table, (B) an ionic compound of a non-coordinating anion and a cation, (C) an organic metal compound of the groups I to III and (D) water, wherein the molar ratio of (C)/(D) is from 0.66 to 5. A novel process for the production of a conjugated diene polymer is also provided, which comprises the polymerization of a conjugated diene compound in the presence of a catalyst comprising (A) a metallocene type complex of a transition metal of the group V of the Periodic Table, (B) an ionic compound of a non-coordinating anion and a cation, (C) an organic metal compound of the groups I to III and (D) water, wherein the molar ratio of (C)/(D) is from 0.66 to 5.

**15 Claims, No Drawings**

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(1) A catalyst comprising (A) a metallocene type complex of a transition metal of the group V of the Periodic table, (B) an ionic compound of a non-coordinating anion and a cation, (C) an organic metal compound of an element of the groups I to III of the Periodic Table and (D) water, wherein the molar ratio of (C)/(D) is from 0.66 to 5.

(2) The catalyst according to Clause (1), wherein said metallocene type complex of a transition metal of the group V of the Periodic table (A) is a compound represented by the following general formula:



wherein R represents a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group or a substituted fluorenyl group; M represents a compound of the group V transition metal; X represents a hydrogen atom, a halogen atom, a C<sub>1-20</sub> hydrocarbon group, an alkoxy group or an amino group; L represents a Lewis base; and n represents 0, 1 or 2.

(3) The catalyst according to Clause (1), wherein said metallocene type complex of a transition metal of the group V of the Periodic table (A) is a compound represented by the following general formula:



wherein R represents a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group or a substituted fluorenyl group; M represents a compound of the group V transition metal; L represents a Lewis base; and n represents 0, 1 or 2.

(4) The catalyst according to any one of Clauses (1) to (3), wherein said transition metal of the group V of the Periodic table is vanadium.

(5) The catalyst according to any one of Clauses (1) to (4), wherein said element of the groups I to III of the Periodic table is aluminum.

(6) A process for the preparation of a conjugated diene polymer, which comprises polymerizing a conjugated diene compound in the presence of a catalyst defined in any one of Clauses (1) to (5).

(7) The process for the preparation of a conjugated diene polymer according to Clause (6), wherein the polymerization of a conjugated diene compound is effected in the presence of hydrogen.

(8) The process for the preparation of a conjugated diene polymer according to Clause (6) or (7), wherein the polymerization of a conjugated diene compound is carried out by bulk polymerization.

(9) The process for the preparation of a conjugated diene polymer according to Clause (6) or (7), wherein the polymerization of a conjugated diene compound is effected in an aromatic compound as a solvent.

(10) The process for the preparation of a conjugated diene polymer according to Clause (6) or (7), wherein the polymerization of a conjugated diene compound is effected in an aliphatic compound as a solvent.

(11) The process for the preparation of a conjugated diene polymer according to Clause (6) or (7), wherein the polymerization of a conjugated diene compound is effected in 2-butene as a solvent.

(12) The process for the preparation of a conjugated diene polymer according to any one of Clauses (8) to (11), wherein said conjugated diene compound is a conjugated diene compound mainly composed of butadiene.

(13) The process for the preparation of a conjugated diene polymer according to Clause (12), wherein said organic

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metal compound of the groups I to III of the Periodic table (C) and said water (D) have previously been allowed to come in contact with each other.

(14) The process for the preparation of a conjugated diene polymer according to Clause (12), wherein said molar ratio of (C)/(D) is from 0.7 to 1.5.

(15) The process for the preparation of a conjugated diene polymer according to Clause (12), wherein the polymerization is preceded by the contact with catalyst components at a temperature of not higher than 40° C. for 1 to 60 minutes.

(16) A polybutadiene obtained by the process for the preparation of a conjugated diene polymer according to Clause (12), wherein the content of 1,2-structure unit, cis-1,4-structure unit and trans-1,4-structure unit in the butadiene monomer unit are from 4 to 30 mol-%, from 65 to 95 mol-% and not more than 5 mol-%, respectively, and the ratio ( $T_{cp}/ML_{1+4}$ ) of toluene solution viscosity ( $T_{cp}$ ) to Mooney viscosity at 100° C. ( $ML_{1+4}$ ) is from 2 to 6.

#### DETAILED DESCRIPTION OF THE INVENTION

Examples of the metallocene type complex of a compound of transition metal of the group V of the Periodic Table include compounds represented by the following general formulae:



In the formulae, n represents 1 or 2; and a represents 0, 1 or 2.

M represents a transition metal of the group V of the Periodic Table. Specific examples of the transition metal include vanadium (V), niobium (Nb), and tantalum (Ta). Preferred among these transition metals is vanadium.

R represents a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group or a substituted fluorenyl group.

Examples of substituents on the substituted cyclopentadienyl group, substituted indenyl group or substituted fluorenyl group include a straight-chain aliphatic hydrocarbon group or branched aliphatic hydrocarbon group such as methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, t-butyl and hexyl, an aromatic hydrocarbon group such as phenyl, tolyl, naphthyl and benzyl, and a hydrocarbon group having silicon atom such as trimethylsilyl. Further examples of the substituted cyclopentadienyl group include those comprising cyclopentadienyl ring connected to part of X with a crosslinking group such as dimethylsilyl, dimethyl methylene, methyl phenyl methylene, diphenyl methylene, ethylene and substituted ethylene.

Specific examples of the substituted cyclopentadienyl group include methyl cyclopentadienyl group, 1,2-dimethyl cyclopentadienyl group, 1,3-dimethyl cyclopentadienyl group, 1,3-di(t-butyl)cyclopentadienyl group, 1,2,3-trimethyl cyclopentadienyl group, 1,2,3,4-tetramethyl cyclopentadienyl group, pentamethyl cyclopentadienyl group, 1-ethyl-2,3,4,5-tetramethyl cyclopentadienyl group, 1-benzyl-2,3,4,5-tetramethyl cyclopentadienyl group,

Examples of tetra-substituted cyclopentadienyl vanadium trichloride include (1,2,3,4-tetramethyl cyclopentadienyl) vanadium trichloride, and (1,2,3,4-tetraphenylcyclopentadienyl)vanadium trichloride.

(vi) Penta-substituted cyclopentadienyl vanadium trichloride

Examples of penta-substituted cyclopentadienyl vanadium trichloride include (pentamethylcyclopentadienyl) vanadium trichloride, (1,2,3,4-tetramethyl-5-phenylcyclopentadienyl)vanadium trichloride, and 1-methyl-2,3,4,5-tetraphenylcyclopentadienyl)vanadium trichloride.

(vii) Indenyl vanadium trichloride

(viii) Substituted indenyl vanadium trichloride

Examples of substituted indenyl vanadium trichloride include (2-methylindenyl)vanadium trichloride, and (2-trimethylsilylindenyl)vanadium trichloride.

(ix) Monoalkoxide, dialkoxide and trialkoxide obtained by substituting chlorine atom in the compounds (i) to (viii) by alkoxy group

Examples of these groups include cyclopentadienyl vanadium tri(tert-butoxide), cyclopentadienyl vanadium tri(isopropoxide), cyclopentadienyl vanadium dimethoxychloride, cyclopentadienyl vanadium di(iso-propoxy)chloride, cyclopentadienyl vanadium di(tert-butoxy)chloride, cyclopentadienyl vanadium di(phenoxy)chloride, cyclopentadienyl vanadium iso-propoxy dichloride, cyclopentadienyl vanadium tert-butoxydichloride, and cyclopentadienyl vanadium phenoxydichloride.

(x) Methylated compound obtained by substituting chlorine atom in the compounds (i) to (ix)

(xi) Compounds comprising R's connected to each other with hydrocarbon group or silyl group

Examples of these compounds include (t-butylamide) dimethyl ( $\eta^5$ -cyclopentadienyl) silane vanadium dichloride, (t-butylamide)dimethyl(trimethyl- $\eta^5$ -cyclopentadienyl) silane vanadium dichloride, (t-butylamide)dimethyl (tetramethyl- $\eta^5$ -cyclopentadienyl)silane vanadium dichloride.

(xii) Dimethylated compounds obtained by substituting chlorine atom in the compounds (xi) by methyl group

(xiii) Monoalkoxylated and dialkoxylated compounds obtained by substituting chlorine atom in the compounds (xi) by alkoxy group

(xiv) Compounds obtained by substituting monochlorinated compounds (xiii) by methyl group

(xv) Amidated compounds obtained by substituting chlorine atom in the compounds (i) to (viii) by amide group

Examples of the amidated compounds include cyclopentadienyl(trisdiethylamide)vanadium, cyclopentadienyl(tris-iso-propylamide)vanadium, cyclopentadienyl(tris-n-octylamide)vanadium, cyclopentadienyl(bisdiethylamide)vanadium chloride, cyclopentadienyl(bis-iso-propylamide)vanadium chloride, cyclopentadienyl(bis-n-octylamide)vanadium chloride, cyclopentadienyl(diethylamide)vanadium dichloride, cyclopentadienyl(iso-propylamide)vanadium dichloride, cyclopentadienyl(n-octylamide)vanadium dichloride, (trimethylsilylcyclopentadienyl)(trisdiethylamide)vanadium, (trimethylsilylcyclopentadienyl) (tris-iso-propylamide) vanadium, (trimethylsilylcyclopentadienyl)(tris-n-octylamide) vanadium, (trimethylsilyl cyclopentadienyl) (bisdiethylamide) vanadium chloride, (trimethylsilylcyclopentadienyl) (bis-iso-propylamide) vanadium chloride, (trimethylsilylcyclopentadienyl) (bis-n-

octylamide)vanadium chloride, (trimethylsilyl cyclopentadienyl)(diethylamide)vanadium dichloride, (trimethylsilylcyclopentadienyl)(iso-propylidene)vanadium dichloride and (trimethylsilylcyclopentadienyl)(n-octylamide)vanadium dichloride.

(xx) Methylated compounds obtained by substituting chlorine atom in the compounds (xv) by methyl group

Specific examples of the compound represented by RM.L<sub>a</sub> include cyclopentadienyl(benzene)vanadium, cyclopentadienyl(toluene)vanadium, cyclopentadienyl(xylene)vanadium, cyclopentadienyl(trimethylbenzene) vanadium, cyclopentadienyl(hexamethylbenzene) vanadium, cyclopentadienyl(naphthalene)vanadium, cyclopentadienyl(anthracene)vanadium, cyclopentadienyl(ferrocene)vanadium, methylcyclopentadienyl (benzene) vanadium, 1,3-dimethyl cyclopentadienyl(benzene) vanadium, 1-butyl-3-methyl cyclopentadienyl(benzene) vanadium, tetramethylcyclopentadienyl(benzene) vanadium, pentamethylcyclopentadienyl(benzene) vanadium, trimethylsilylcyclopentadienyl(benzene) vanadium, 1,2-bis(trimethylsilyl)cyclopentadienyl(benzene) vanadium, 1,3-bis(trimethylsilyl)cyclopentadienyl(benzene) vanadium, indenyl (benzene)vanadium, 2-methylindenyl (benzene)vanadium, 2-trimethylsilylindenyl(benzene) vanadium, fluorenyl(benzene)vanadium, cyclopentadienyl(ethylene)(trimethylphosphine)vanadium, cyclopentadienyl(butadiene)(trimethylphosphine)vanadium, cyclopentadienyl(1,4-diphenylbutadiene) (trimethylphosphine)vanadium, cyclopentadienyl(1,1,4,4-tetraphenylbutadiene)(trimethylphosphine)vanadium, cyclopentadienyl(2,3-dimethylbutadiene) (trimethylphosphine)vanadium, cyclopentadienyl(2,4-hexadiene)(trimethylphosphine)vanadium, cyclopentadienyl tetracarbonyl vanadium, and indenyl tetracarbonyl vanadium.

Specific examples of the compound represented by R<sub>n</sub>MX<sub>2-n</sub>.L<sub>a</sub> wherein n is 1 include those having other  $\sigma$ -connecting ligands hydrogen atom, halogen atoms such as chlorine, bromine and iodine, hydrocarbon groups such as methyl, phenyl, benzyl, neopentyl, trimethylsilyl and bistrimethylsilylmethyl, hydrocarbon oxy groups such as methoxy, ethoxy and iso-propoxy or hydrocarbon amino groups such as dimethylamino, diethylamino, di-iso-propylamino and dioctylamino.

Specific examples of the compound represented by R<sub>n</sub>MX<sub>2-n</sub>.L<sub>a</sub> wherein n is 2 include those having various cycloalkadienyl rings connected to each other with a crosslinking group such as Me<sub>2</sub>Si, dimethylmethylene, methylphenylmethylene, diphenylmethylene, ethylene and substituted ethylene.

Other examples of ligands which can be incorporated in the compound represented by R<sub>n</sub>MX<sub>2-n</sub>.L<sub>a</sub> include neutral Lewis bases such as olefin, diene, aromatic hydrocarbon, alkyne, amine, amide, phosphine, ether, ketone and ester. Preferred among these ligands are Lewis bases free of active hydrogen.

Specific examples of the compound represented by R<sub>n</sub>MX<sub>2-n</sub>.L<sub>a</sub> wherein n is 1 include chlorocyclopentadienyl (tetrahydrofuran)vanadium, chlorocyclopentadienyl (trimethylphosphine)vanadium, chlorocyclopentadienyl bis (trimethylphosphine)vanadium, chlorocyclopentadienyl (1,2-bisdimethylphosphinoethane)vanadium, chlorocyclopentadienyl(1,2-bisdiphenylphosphinoethane) vanadium, chlorocyclopentadienyl(triphenylphosphine) vanadium, chlorocyclopentadienyl(tetrahydrothiophene) vanadium, bromocyclopentadienyl(tetrahydrofuran) vanadium, iodocyclopentadienyl(tetrahydrofuran)



dium dichloride, (1,3-bis(trimethyl silyl)cyclopentadienyl)oxo vanadium dichloride, indenyl oxo vanadium dichloride, (2-methylindenyl)oxo vanadium dichloride, (2-trimethylsilylindenyl)oxo vanadium dichloride, and fluorenyl oxo vanadium dichloride.

Other examples of the compound represented by  $RM(O)X_2$  include dimethylated compounds obtained by substituting chlorine atom in the foregoing compounds by methyl group.

Further examples of the compound represented by  $RM(O)X_2$  include those wherein R and X are connected to each other with a hydrocarbon or silyl group. Examples of these compounds include amidechloride compounds such as (t-butylamide) dimethyl ( $\eta^5$ -cyclopentadienyl) silaneoxo vanadium chloride and (t-butylamide)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silaneoxo vanadium chloride, and methylated compounds obtained by substituting chlorine atom in these compounds by methyl group.

Further examples of these compounds include cyclopentadienyl oxo vanadium dimethoxide, cyclopentadienyl oxo vanadium di(iso-propoxide), cyclopentadienyl oxo vanadium di(tert-butoxide), cyclopentadienyl oxo vanadium diphenoxide, cyclopentadienyl oxo vanadium methoxychloride, cyclopentadienyl oxo vanadium iso-propoxychloride, cyclopentadienyl oxo vanadium tert-butoxychloride, and cyclopentadienyl oxo vanadium phenoxychloride.

Other examples of these compounds include methylated compounds obtained by substituting chlorine atom in the foregoing various compounds by methyl group.

Examples of these compounds include

(cyclopentadienyl)(bisdiethylamide)oxo vanadium,

(cyclopentadienyl)(bisdiisopropylamide)oxo vanadium, and

(cyclopentadienyl)(bisdi-n-octylamide)oxo vanadium.

Specific examples of the compound represented by  $R_nMX_{3-n}(NR')$  include cyclopentadienyl (methylimide) vanadium dichloride, cyclopentadienyl(phenylimide) vanadium dichloride, cyclopentadienyl(2,6-dimethylphenylimide)vanadium dichloride, cyclopentadienyl(2,6-di-iso-propyl phenylimide)vanadium dichloride, (methylcyclopentadienyl)(phenylimide) vanadium dichloride, (1,3-dimethyl cyclopentadienyl) (phenylimide)vanadium dichloride, (1-butyl-3-methylcyclopentadienyl)(phenylimide)vanadium dichloride, (pentamethylcyclopentadienyl)(phenylimide) vanadium dichloride, indenyl(phenylimide)vanadium dichloride, 2-methylindenyl(phenylimide)vanadium dichloride, and fluorenyl(phenylimide)vanadium dichloride.

Other examples of the compound represented by  $R_nMX_{3-n}(NR')$  include those wherein R and X are connected to each other with a hydrocarbon or silyl group. Examples of these compounds include amidechloride compounds such as (t-butylamide)dimethyl( $\eta^5$ -cyclopentadienyl)silane(phenylimide)vanadium chloride and (t-butylamide)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane(phenylimide)vanadium chloride, and methylated compounds obtained by substituting chlorine atom in these compounds by methyl group.

Further examples of the compound represented by  $R_nMX_{3-n}(NR')$  include those wherein R's are connected to each other with a hydrocarbon or silyl group. Examples of these compounds include imidechloride compounds such as dimethylbis( $\eta^5$ -cyclopentadienyl)silane(phenylimide) vanadium chloride, dimethylbis( $\eta^5$ -cyclopentadienyl)silane

(tolylimide)vanadium chloride, dimethylbis(tetramethyl- $\eta^5$ -cyclopentadienyl)silane(phenylimide)vanadium chloride and dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane (tolylimide)vanadium chloride, and methylated compounds obtained by substituting chlorine atom in these compounds by methyl group.

Further examples of these compounds include cyclopentadienyl vanadium(phenylimide)dimethoxide, cyclopentadienyl vanadium(phenylimide)di-iso-propoxide, cyclopentadienyl vanadium(phenylimide)(iso-propoxy)chloride, (cyclopentadienyl)(bisdiethylamide)vanadium (phenylimide), and (cyclopentadienyl)(bis-iso-propylamide) vanadium(phenylimide).

Examples of the non-coordinating anion constituting the ionic compound made of a non-coordinating anion and a cation in the component (B) of the present invention include tetra(phenyl)borate, tetra(fluorophenyl)borate, tetrakis (difluorophenyl)borate, tetrakis(trifluorophenyl)borate, tetrakis(tetrafluorophenyl)borate, tetrakis(pentafluorophenyl)borate, tetrakis(tetrafluoromethylphenyl) borate, tetrakis(3,5-bistrifluoromethylphenyl)borate, tetra (tolyl)borate, tetra(xyl)borate, triphenyl (pentafluorophenyl)borate, tris(pentafluorophenyl)(phenyl) borate, tridecahydride-7,8-dicarbaundecaborate, tetrafluoroborate, and hexafluorophosphate.

On the other hand, examples of the cation constituting the ionic compound made of a non-coordinating anion and a cation in the component (B) of the present invention include carbonium cation, oxonium cation, ammonium cation, phosphonium cation, cycloheptatrienyl cation, and ferrocenium cation containing transition metal.

Specific examples of the carbonium cation include trisubstituted carbonium cations such as triphenyl carbonium cation and tri-substituted phenyl carbonium cation. Specific examples of the tri-substituted phenylcarbonium cation include tri(methylphenyl)carbonium cation, and tris (dimethyl phenyl)carbonium cation.

Specific examples of the ammonium cation include trialkyl ammonium cations such as trimethyl ammonium cation, triethyl ammonium cation, tripropyl ammonium cation, tri(i-butyl)ammonium cation and tri(n-butyl) ammonium cation, N,N-dialkyl anilinium cations such as N,N-dimethyl anilinium cation, N,N-diethyl anilinium cation and N,N-2,4,6-pentamethyl anilinium cation, and dialkyl ammonium cations such as di(i-propyl)ammonium cation and dicyclohexyl ammonium cation.

Specific examples of the phosphonium cation include triaryl phosphonium cations such as triphenyl phosphonium cation, tri(methylphenyl)phosphonium cation and tris (dimethylphenyl)phosphonium cation.

As the foregoing ionic compound there may be preferably used one comprising in combination components arbitrarily selected from the group consisting of the foregoing non-coordinating anions and cations.

Preferred examples of the ionic compound include triphenylcarbonium tetrakis(pentafluorophenyl)borate, triphenylcarbonium tetrakis(3,5-bistrifluoromethylphenyl)borate, triphenylcarbonium tetrakis(fluorophenyl)borate, N,N-dimethylanilium tetrakis(pentafluorophenyl)borate, N,N-dimethylanilium tetrakis(3,5-bistrifluoromethylphenyl) borate, and 1,1'-dimethylferrocenium tetrakis (pentafluorophenyl)borate.

These ionic compounds may be used singly or in combination of two or more thereof.

Examples of the organic metal compound of element of the group I to III of the Periodic Table as the component (C) of the present invention include organic aluminum

erably from 10 minutes to 12 hours, even more preferably from 10 minutes to 6 hours, particularly from 30 minutes to 6 hours.

The material to be polymerized is subjected to polymerization for a predetermined period of time. If necessary, a stopper such as alcohol is then added to terminate the polymerization. If necessary, the pressure in the polymerization tank is relaxed. The product is then subjected to post-treatment such as washing and drying.

The use of the polymerization process of the present invention makes it possible to produce a polybutadiene having a 1,2-structure content of from 4 to 30%, preferably from 5 to 25%, more preferably from 5 to 20%, particularly from 7 to 15%, a cis-1, 4-structure content of from 65 to 95%, preferably from 70 to 95%, more preferably from 70 to 92%, and a trans-1,4-structure content of not more than 5%, preferably not more than 4.5%, particularly from 0.5 to 4.0%.

If the microstructure falls outside the above defined range, the resulting polymer leaves something to be desired in reactivity (graft reactivity or crosslinking reactivity). If used as an additive or the like, the polymer gives deteriorated rubber properties, disadvantageously affecting the balance of physical properties and external appearance.

In accordance with the polymerization process of the present invention, a polybutadiene having an intrinsic viscosity  $[\eta]$  of from 0.1 to 20 as determined in toluene at 30° C. can be produced.

Further, the use of the polymerization process of the present invention makes it possible to produce a polybutadiene having a weight-average molecular weight of from 10,000 to 4,000,000 as determined by GPC with polystyrene as a standard substance.

The polybutadiene produced according to the present invention exhibits a  $T_{cp}/ML_{1+4}$  ratio of from 2 to 6, preferably from 2.5 to 5 wherein  $T_{cp}$  is toluene solution viscosity and  $ML_{1+4}$  is Mooney viscosity at 100° C.

The toluene solution viscosity ( $T_{cp}$ ) of the polybutadiene of the present invention is from 20 to 500, preferably from 30 to 350.

The Mooney viscosity ( $ML_{1+4}$ ) of the polybutadiene of the present invention is from 10 to 200, preferably from 20 to 100.

The molecular weight of the polybutadiene of the present invention is from 0.1 to 10, preferably from 0.1 to 5, as calculated in terms of intrinsic viscosity  $[\eta]$  determined in toluene at 30° C.

These polybutadienes can be preferably used as an impact modifier for polystyrene.

The monomer to be polymerized is preferably allowed to come in contact with the foregoing catalyst components at a temperature of 40° C. for 1 to 60 minutes before polymerization. In other words, the monomer to be polymerized is preferably subjected to prepolymerization at a predetermined temperature in the presence of the foregoing catalyst. The prepolymerization of the present invention can be accomplished by gas phase process, slurry process, bulk process or the like. The solid matter obtained in the prepolymerization process may or may not be separated before the subsequent polymerization.

The prepolymerization time is normally not more than 600 minutes, preferably not more than 120 minutes, more preferably from 30 seconds to 120 minutes. If the prepolymerization time falls outside the above defined range, it is disadvantageous in that the subsequent polymerization is effected at an insufficient activity.

The prepolymerization is effected in the presence of the various catalyst components at a temperature of not higher

than 40° C., preferably from -100° C. to 40° C., more preferably from -50° C. to 40° C. If the prepolymerization temperature falls outside the above defined range, the subsequent polymerization is effected at a remarkably lowered activity. Further, polymerization proceeds too far during the prepolymerization, giving a process problem.

During the prepolymerization, hydrogen may be present as necessary. The amount of hydrogen to be present in the polymerization is preferably not more than 500 mmol or not more than 12 liter at 20° C. and 1 atm., more preferably not more than 50 mmol or not more than 1.2 liter at 20° C. and 1 atm., particularly from 0.005 to 20 mmol or from 0.0001 to 0.48 liter at 20° C. and 1 atm. based on 1 mol of the conjugated diene used.

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto.

The microstructure of polybutadiene was analyzed by infrared absorption spectroscopy. In some detail, the microstructure of polybutadiene was calculated from the ratio of absorption intensity at 740  $\text{cm}^{-1}$  for cis-1,4-structure, 967  $\text{cm}^{-1}$  for trans-1,4-structure and 911  $\text{cm}^{-1}$  for 1,2-structure (vinyl).

For the evaluation of molecular weight distribution, the ratio of  $M_w/M_n$  was determined wherein  $M_w$  is weight-average molecular weight determined by GPC with polystyrene as a standard substance and  $M_n$  is number-average molecular weight.

The intrinsic viscosity  $[\eta]$  of polybutadiene was determined in toluene solution at 30° C.

Mooney viscosity ( $ML_{1+4}$ ) of the polymer was determined in accordance with JIS K 6300.

Toluene solution viscosity ( $T_{cp}$ ) of the polymer was determined by dissolving 2.28 g of the polymer in 50 ml of toluene, and subjecting the toluene solution of the polymer to the viscosity measurement by a Canon Fenske viscometer No. 400 using a viscometer-correction standard liquid in accordance with JIS Z 8809 at a temperature of 25° C.

## EXAMPLES 1 TO 14

Into a 1.5 liter autoclave in which the air within had been replaced by nitrogen was charged 400 ml (248 g) of 1,3-butadiene. The material was then stirred. To the material was then added water ( $\text{H}_2\text{O}$ ) as set forth in Table 1. The mixture was then stirred for 30 minutes to make a solution. Subsequently, hydrogen gas was introduced into the autoclave in an amount of 200 ml as determined at 20° C. and 1 atm. by an integrating mass flow meter. Subsequently, triethyl aluminum (1 mmol/ml toluene solution) was added to the mixture in an amount as set forth in Table 1. After 3 minutes, 0.8 ml of cyclopentadienyl vanadium trichloride ( $\text{CpVCl}_3$ ) (0.005 mmol/ml toluene solution) was added to the mixture. 4 ml of triphenylcarbonium tetrakis (pentafluorophenyl)borate ( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ ) (0.0025 mmol/ml toluene solution) was then added to the mixture. The mixture was then subjected to polymerization at a temperature of 40° C. for a period of time set forth in Table 1.

After polymerization, a mixture of equal part of ethanol and heptane containing a small amount of 2,6-di-*t*-butyl-p-cresol was added to the product. The pressure in the autoclave was then relaxed. The product was poured into ethanol to precipitate a polymer which was then withdrawn by filtration and dried. The results of polymerization are set forth in Tables 2 and 3.

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the base water content was 4 mg. This value was taken into account to calculate TEA/H<sub>2</sub>O ratio in the following examples.

## EXAMPLES 19 TO 23

Into a 1.5 liter autoclave in which the air within had been replaced by nitrogen was charged 1.0 liter of 1,3-butadiene through a molecular sieve. The material was then stirred. To the material was then added water as set forth in Table 8. The mixture was then stirred for 30 minutes to make a solution. Subsequently, hydrogen gas was introduced into the butadiene in an amount of 200 ml as determined at 20° C. and 1 atm. by an integrating mass flow meter. Subsequently, triethyl aluminum (1 mmol/ml toluene solution) was added to the mixture in an amount as set forth in Table 8. After 10 minutes of stirring, 2.5 ml of cyclopentadienyl vanadium trichloride (CpVCl<sub>3</sub>) (0.005 mmol/ml toluene solution) and 10 ml of triphenylcarbonium tetrakis(pentafluorophenyl) borate (Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) (0.0025 mmol/ml toluene solution) were added to the mixture in the order as set forth in Table 9. The mixture was then subjected to polymerization at a temperature of 40° C. for 30 minutes.

After polymerization, a mixture of equal part of ethanol and heptane containing a small amount of 2,6-di-t-butyl-p-cresol was added to the product. The pressure in the autoclave was then relaxed. The product was poured into ethanol to precipitate a polymer which was then withdrawn by filtration and dried. The results of polymerization are set forth in Tables 9 and 10.

## EXAMPLES 24 TO 28

Into a 1.5 liter autoclave in which the air within had been replaced by nitrogen was charged 1.0 liter of 1,3-butadiene through a molecular sieve. The material was then stirred. Subsequently, hydrogen gas was introduced into the butadiene in an amount of 200 ml as determined at 20° C. and 1 atm. by an integrating mass flow meter. Subsequently, triethyl aluminum (1 mmol/ml toluene solution) was added to the mixture in an amount as set forth in Table 8. The mixture was then stirred for 10 minutes. Water was then added to the mixture with stirring in an amount set forth in Table 8. After 30 minutes of stirring, 2.5 ml of cyclopentadienyl vanadium trichloride (CpVCl<sub>3</sub>) (0.005 mmol/ml toluene solution) and 10 ml of triphenylcarbonium tetrakis(pentafluorophenyl)borate (Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) (0.0025 mmol/ml toluene solution) were added to the mixture in the order as set forth in Table 9. The mixture was then subjected to polymerization at a temperature of 40° C. for 30 minutes.

After polymerization, a mixture of equal part of ethanol and heptane containing a small amount of 2,6-di-t-butyl-p-cresol was added to the product. The pressure in the autoclave was then relaxed. The product was poured into ethanol to precipitate a polymer which was then withdrawn by filtration and dried. The results of polymerization are set forth in Tables 9 and 10.

## COMPARATIVE EXAMPLES 1 AND 2

The procedure of Examples 19 to 23 was followed to obtain 1 liter of 1,3-butadiene having a controlled 1,3-

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butadiene content. Hydrogen gas was introduced into the 1,3-butadiene in an amount of 200 ml as determined at 20° C. and 1 atm. by an integrating mass flow meter. Subsequently, 2.5 ml of cyclopentadienyl vanadium trichloride (CpVCl<sub>3</sub>) (0.005 mmol/ml toluene solution) and 10 ml of triphenylcarbonium tetrakis(pentafluorophenyl)borate (Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) (0.0025 mmol/ml toluene solution) were added to the mixture in the order as set forth in Table 9. To the mixture was then added triethyl aluminum (1 mmol/ml toluene solution) in an amount as set forth in Table 8. After 10 minutes of stirring, the mixture was then subjected to polymerization at a temperature of 40° C. for 30 minutes.

After polymerization, a mixture of equal part of ethanol and heptane containing a small amount of 2,6-di-t-butyl-p-cresol was added to the product. The pressure in the autoclave was then relaxed. The product was poured into ethanol to precipitate a polymer which was then withdrawn by filtration and dried. The results of polymerization are set forth in Tables 9 and 10.

## COMPARATIVE EXAMPLES 3 AND 4

The procedure of Examples 24 to 28 was followed except that triethyl aluminum (1 mmol/ml toluene solution) was added in an amount as set forth in Table 8. After 10 minutes of stirring, 2.5 ml of cyclopentadienyl vanadium trichloride (CpVCl<sub>3</sub>) (0.005 mmol/ml toluene solution) and 10 ml of triphenylcarbonium tetrakis(pentafluorophenyl) borate (Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) (0.0025 mmol/ml toluene solution) were added to the mixture in the order as set forth in Table 9. Water was then added to the mixture with stirring as set forth in Table 8. After 10 minutes of stirring, the mixture was then subjected to polymerization at a temperature of 40° C. for 30 minutes.

After polymerization, a mixture of equal part of ethanol and heptane containing a small amount of 2,6-di-t-butyl-p-cresol was added to the product. The pressure in the autoclave was then relaxed. The product was poured into ethanol to precipitate a polymer which was then withdrawn by filtration and dried. The results of polymerization are set forth in Tables 9 and 10.

TABLE 7

Reference Example No.	Added water (mg)	H <sub>2</sub> O	
		Water content in butadiene (ppm)	Base water content (mg)
1	10	14	4
2	20	25	5
3	30	34	4
4	40	43	3
5	50	54	4

TABLE 11

Example No.	Added water (mg)	Water content in butadiene (ppm)	H <sub>2</sub> O (D) (mmol)	TEA (C) (mmol)	TEA/H <sub>2</sub> O (C)/(D) (total content in butadiene)	Polymeri- zation time (min.)
Example 29	6	10	0.55	0.45	0.81	30
Example 30	6	10	0.55	0.55	0.99	30
Example 31	6	10	0.55	0.65	1.17	30
Example 32	6	10	0.55	0.75	1.35	30
Example 33	6	10	0.55	1.25	2.25	30
Example 34	6	10	0.55	2	3.60	30
Comparative Example 5	6	10	0.55	3.13	5.64	30
Comparative Example 6	6	10	0.55	3.13	5.64	30
Comparative Example 7	6	10	0.55	3.13	5.64	30

\*Base water content: 4 mg

TABLE 12

Example No.	Order of addition	Yield (g)
Example 29	(D) → (C) → (A) → (B)	108
Example 30	(D) → (C) → (A) → (B)	139
Example 31	(D) → (C) → (A) → (B)	155
Example 32	(D) → (C) → (A) → (B)	79
Example 33	(D) → (C) → (B) → (A)	34
Example 34	(D) → (C) → (A) → (B)	19
Comparative Example 5	(D) → (C) → (A) → (B)	6
Comparative Example 6	(D) → (C) → (A) → (B)	28
Comparative Example 7	(D) → (C) → (A) → (B)	88

## REFERENCE EXAMPLES 6 TO 10

Firstly, the amount of water content present in a 1.5 liter autoclave was measured in accordance with the following procedure.

## Measurement Procedure

Into a 1.5 liter autoclave in which the air within had been replaced by nitrogen was charged 1.0 liter of a solution of 300 ml of toluene, 400 ml of cis-2-butene and 300 ml (184 g) of 1,3-butadiene through a molecular sieve. The mixture was then stirred. Subsequently, water was added to the mixture as set forth in Table 13. The mixture was then stirred for 30 minutes to make a solution. The solution was then measured for water content by means of a Karl Fischer moisture meter. The results of water content in FB (solvent+butadiene) are set forth in Table 13.

The same procedure as used above was then effected with different amounts of water added five times in total. The base water content was then calculated from the difference between the foregoing water content in FB and the added amount of water averaged over five times. As a result, the base water content was 4 mg. This value was taken into account to calculate TEA/H<sub>2</sub>O ratio in the following examples.

## EXAMPLES 35 TO 37

Into a 1.5 liter autoclave in which the air within had been replaced by nitrogen was charged 1.0 liter of a solution of 300 ml of toluene, 400 ml of cis-2-butene and 300 ml (184 g) of 1,3-butadiene through a molecular sieve. The material was then stirred. To the material was then added water as set forth in Table 14. The mixture was then stirred for 30 minutes to make a solution. Subsequently, hydrogen gas was

introduced into FB (solvent+butadiene) in an amount of 130 ml as determined at 20° C. and 1 atm. by an integrating mass flow meter. Subsequently, triethyl aluminum (1 mmol/ml toluene solution) was added to the mixture in an amount as set forth in Table 14. After 10 minutes of stirring, 1.6 ml of cyclopentadienyl vanadium trichloride (CpVCl<sub>3</sub>) (0.005 mmol/ml toluene solution) and 6.4 ml of triphenylcarbonium tetrakis(pentafluorophenyl)borate (Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) (0.0025 mmol/ml toluene solution) were added to the mixture in the order as set forth in Table 15. The mixture was then subjected to polymerization at a temperature of 60° C. for 30 minutes.

After polymerization, a mixture of equal part of ethanol and heptane containing a small amount of 2,6-di-t-butyl-p-cresol was added to the product. The pressure in the autoclave was then relaxed. The product was poured into ethanol to precipitate a polymer which was then withdrawn by filtration and dried. The results of polymerization are set forth in Tables 15 and 16.

## EXAMPLES 38 TO 42

Into a 1.5 liter autoclave in which the air within had been replaced by nitrogen was charged 1.0 liter of a solution of 300 ml of toluene, 400 ml of cis-2-butene and 300 ml (184 g) of 1,3-butadiene through a molecular sieve. The material was then stirred. Subsequently, hydrogen gas was introduced into the butadiene in an amount of 130 ml as determined at 20° C. and 1 atm. by an integrating mass flow meter. Subsequently, triethyl aluminum (1 mmol/ml toluene solution) was added to the mixture in an amount as set forth in Table 14. The mixture was then stirred for 10 minutes. Water was then added to the mixture with stirring in an amount set forth in Table 14. After 30 minutes of stirring, 1.6 ml of cyclopentadienyl vanadium trichloride (CpVCl<sub>3</sub>) (0.005 mmol/ml toluene solution) and 6.4 ml of triphenylcarbonium tetrakis(pentafluorophenyl)borate (Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) (0.0025 mmol/ml toluene solution) were added to the mixture in the order as set forth in Table 15. The mixture was then subjected to polymerization at a temperature of 60° C. for 30 minutes.

After polymerization, a mixture of equal part of ethanol and heptane containing a small amount of 2,6-di-t-butyl-p-cresol was added to the product. The pressure in the autoclave was then relaxed. The product was poured into ethanol to precipitate a polymer which was then withdrawn by filtration and dried. The results of polymerization are set forth in Tables 15 and 16.

## COMPARATIVE EXAMPLE 8

Into a 1.5 liter autoclave in which the air within had been replaced by nitrogen were charged 1.0 liter of a solution of

TABLE 16-continued

Example No.	[ $\eta$ ]	Microstructure (%)		
		Cis	Trans	1,2-
Example 8	0.88	87.6	1.1	11.3
Comparative Example 9				
Comparative Example 10	0.98	87.3	1.4	11.3

#### EXAMPLES 43 TO 50 AND COMPARATIVE EXAMPLES 11 TO 14

Into a 1.5 liter autoclave in which the air within had been replaced by nitrogen was charged 1.0 liter of a solution of 300 ml of toluene, 400 ml of cis-2-butene and 300 ml (184 g) of 1,3-butadiene through a molecular sieve. The material was then stirred. Subsequently, to the mixture was added water as set forth in Table 17. The mixture was then stirred for 30 minutes. Hydrogen gas was then introduced into FB (solvent+butadiene) in an amount of 130 ml as determined at 20° C. and 1 atm. by an integrating mass flow meter. Subsequently, triethyl aluminum (1 mmol/ml toluene solution) was added to the mixture in an amount as set forth in Table 17. The mixture was then stirred for 10 minutes. After 10 minutes of stirring, 1.6 ml of cyclopentadienyl vanadium trichloride ( $\text{CpVCl}_3$ ) (0.005 mmol/ml toluene solution) and 6.4 ml of triphenylcarbonium tetrakis(pentafluorophenyl)borate ( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ ) (0.0025 mmol/

#### EXAMPLES 51 TO 54 AND COMPARATIVE EXAMPLE 15

Into a 1.5 liter autoclave in which the air within had been replaced by nitrogen was charged 1.0 liter of a solution of 300 ml of toluene, 400 ml of cis-2-butene and 300 ml (184 g) of 1,3-butadiene through a molecular sieve. The material was then stirred. Hydrogen gas was then introduced into the material in an amount of 130 ml as determined at 20° C. and 1 atm. by an integrating mass flow meter. Subsequently, triethyl aluminum (1 mmol/ml toluene solution) was added to the mixture in an amount as set forth in Table 17. The mixture was then stirred for 10 minutes. Water was then added to the mixture with stirring in an amount set forth in Table 17. After 30 minutes of stirring, 1.6 ml of cyclopentadienyl vanadium trichloride ( $\text{CpVCl}_3$ ) (0.005 mmol/ml toluene solution) and 6.4 ml of triphenylcarbonium tetrakis(pentafluorophenyl)borate ( $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ ) (0.0025 mmol/ml toluene solution) were added to the mixture in the order as set forth in Table 18. The mixture was then subjected to polymerization at a temperature of 60° C. for 30 minutes.

After polymerization, a mixture of equal part of ethanol and heptane containing a small amount of 2,6-di-t-butyl-p-cresol was added to the product. The pressure in the autoclave was then relaxed. The product was poured into ethanol to precipitate a polymer which was then withdrawn by filtration and dried.

The results of polymerization are set forth in Tables 18 and 19.

TABLE 17

Example No.	$\text{H}_2\text{O}$ (D)			TEA (C) (mmol)	$\text{TEA}/\text{H}_2\text{O}$ (C)/(D) (total amount in FB)	Polymeri- zation time (min.)
	Added water (mg)	Water content in FB (ppm)	mmol			
Example 43	18	22	1.22	1	0.82	30
Example 44	16	20	1.11	1	0.90	30
Example 45	14	18	1.00	1	1.00	30
Example 46	10	14	0.78	1	1.29	30
Example 47	8	12	0.67	1	1.50	30
Example 48	36	40	2.22	2	0.90	30
Example 49	25	29	1.61	2	1.24	30
Example 50	20	24	1.33	2	1.50	30
Example 51	16	20	1.11	1	0.90	30
Example 52	14	18	1.00	1	1.00	30
Example 53	10	14	0.78	1	1.29	30
Example 54	8	12	0.67	1	1.50	30
Comparative Example 11	4	8	0.44	1	2.25	30
Comparative Example 12	68	72	4.00	2	0.50	30
Comparative Example 13	10.4	14.4	0.80	2	2.50	30
Comparative Example 14	9	13	0.72	2	2.77	30
Comparative Example 15	3.2	7.2	0.40	1	2.50	30

\*Base water content: 4 mg

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ml toluene solution) were added to the mixture in the order as set forth in Table 18. The mixture was then subjected to polymerization at a temperature of 60° C. for 30 minutes.

After polymerization, a mixture of equal part of ethanol and heptane containing a small amount of 2,6-di-t-butyl-p-cresol was added to the product. The pressure in the autoclave was then relaxed. The product was poured into ethanol to precipitate a polymer which was then withdrawn by filtration and dried.

The results of polymerization are set forth in Tables 18 and 19.

TABLE 18

Example No.	Order of addition	Yield (g)
Example 43	(D) → (C) → (A) → (B)	89
Example 44	(D) → (C) → (A) → (B)	121
Example 45	(D) → (C) → (A) → (B)	126
Example 46	(D) → (C) → (A) → (B)	107
Example 47	(D) → (C) → (A) → (B)	94
Example 48	(D) → (C) → (A) → (B)	95
Example 49	(D) → (C) → (A) → (B)	101

65

TABLE 21

Example No.	Yield		Microstructure (%)		
	(g)	[ $\eta$ ]	Cis	Trans	1,2-
Example 55	77	2.07	88.0	1.3	10.7
Example 56	86	2.12	88.0	1.3	10.7
Example 57	75	1.98	88.1	1.2	10.7
Example 58	84	2.13	88.0	1.3	10.7
Example 59	79	2.26	88.0	1.3	10.7
Example 60	65	2.03	88.1	1.3	10.7
Example 61	78	2.00	87.9	1.3	10.8
Example 62	68	1.91	87.9	1.3	10.8
Comparative Example 16	56	1.86	87.9	1.2	10.9
Comparative Example 17	53	1.59	87.7	1.4	10.9
Comparative Example 18	26	1.24	87.9	1.2	10.9

As has been mentioned above, the present invention provides a process for the production of a conjugated diene polymer having a controlled microstructure at a high polymerization activity in the presence of a metallocene type complex of compound of transition metal of the group V of the Periodic Table. The present invention also provides a process for the production of a polybutadiene having a microstructure comprising a high cis-structure having 1,2-structure properly incorporated therein and hence little trans-structure at a high activity. The present invention further provides a polybutadiene having a microstructure comprising a high cis-structure having 1,2-structure properly incorporated therein and hence little trans-structure and a high linearity.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A process for the preparation of a conjugated diene polymer, which comprises polymerizing a conjugated diene compound in the presence of a catalyst comprising (A) a metallocene complex of a transition metal of the group V of the Periodic Table, (B) an ionic compound of a non-coordinating anion and a cation, (C) an organic metal compound of an element of the groups I to III of the Periodic Table and (D) water, wherein the molar ratio of (C)/(D) is from 0.7:1 to 1.5:1.

2. The process for the preparation of a conjugated diene polymer according to claim 1, wherein said metallocene complex of a transition metal of the group V of the Periodic table (A) is a compound represented by the following general formula:



wherein R represents a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group or a substituted fluorenyl group; M represents a compound of the group V transition metal; X represents a hydrogen atom, a halogen atom, a C<sub>1-20</sub> hydrocarbon group, an alkoxyl group or an amino group; L represents a Lewis base; and a represents 0, 1 or 2.

3. The process for the preparation of a conjugated diene polymer according to claim 1, wherein said metallocene complex of a transition metal of the group V of the Periodic table (A) is a compound represented by the following general formula:



wherein R represents a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group or a substituted fluorenyl group; M represents a compound of the group V transition metal; L represents a Lewis base; and a represents 0, 1 or 2.

4. The process for the preparation of a conjugated diene polymer according to claim 1, wherein said transition metal of the group V of the Periodic table is vanadium.

5. The process for the preparation of a conjugated diene polymer according to claim 1, wherein said element of the groups I to III of the Periodic table is aluminum.

6. The process for the preparation of a conjugated diene polymer according to claim 1, wherein the polymerization of a conjugated diene compound is effected in the presence of hydrogen.

7. The process for the preparation of a conjugated diene polymer according to claim 1, wherein the polymerization of a conjugated diene compound is carried out by bulk polymerization.

8. The process for the preparation of a conjugated diene polymer according to claim 1, wherein the polymerization of a conjugated diene compound is effected in an aromatic compound as a solvent.

9. The process for the preparation of a conjugated diene polymer according to claim 1, wherein the polymerization of a conjugated diene compound is effected in an aliphatic compound as a solvent.

10. The process for the preparation of a conjugated diene polymer according to claim 1, wherein the polymerization of a conjugated diene compound is effected in 2-butene as a solvent.

11. The process for the preparation of a conjugated diene polymer according to claim 1, wherein said conjugated diene compound is a conjugated diene compound mainly composed of butadiene.

12. The process for the preparation of a conjugated diene polymer according to claim 1, wherein said organic metal compound of the groups I to III of the Periodic table (C) and said water (D) have previously been allowed to come in contact with each other.

13. The process for the preparation of a conjugated diene polymer according to claim 1, wherein the polymerization is preceded by the contact with a catalyst component at a temperature of not higher than 40° C. for 1 to 60 minutes.

14. The process for the preparation of a conjugated diene polymer according to claim 1, wherein within 30 minutes after contacting (C) said organic metal compound of the groups I to III of the periodic table with (D) said water, other catalyst components are added to the mixture.

15. The process for the preparation of a conjugated diene polymer according to claim 1, wherein the organic metal compound is selected from the group consisting of triethyl aluminum and triisobutyl aluminum.

\* \* \* \* \*